PERVAPORATION OF ETHANOL-WATER MIXTURE USING PVA ZEOLITE-CLAY MEMBRANES

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Abstract. The objective of this research is to study the effects of feed concentration and temperature on the pervaporation of ethanol-water mixtures using polyvinyl alcohol (PVA) zeolite-clay membranes. The liquid feeds for the pervaporation were prepared using different weight concentrations of ethanol which were 10 wt%, 30 wt%, 50 wt%, 70 wt% and 90 wt% of ethanol. The pervaporation separations were conducted at different temperatures which were 30, 40, 50, 60 and 70 °C. The PVA zeolite-clay membranes were prepared by dissolving 0.2 wt% zeolite-clay powder and 5 wt% PVA powder in distilled water. The solution was casted on a porous support to produce composite membrane. The support layers were produced through phase inversion process using casting-solution of 12 wt% polysulfone, 11 wt% methyl cellusolve and 77 wt% N,N-dimethylformamide (DMF). The membranes were used for the separation of ethanol-water mixtures via pervaporation. The results showed that, when the ethanol concentrations of feed and feed temperature increased, the selectivity increased but absorption (flux) decreased. The PVA zeolite- clay composite membranes were relatively hydrophilic, mechanically strong and thus suitable to be used for the pervaporation separation of ethanol-water mixtures.

Keywords: Pervaporation; PVA membrane; polysulfone membrane; zeolite-clay; ethanol-water mixtures

Abstrak. Penyelidikan ini bertujuan untuk mengkaji pengaruh bagi kepekatan masukan dan suhu dalam proses pervaporasi dengan menggunakan membran PVA zeolit tanah liat komposit yang dihasilkan bagi pemisahan campuran larutan ethanol-air. Komposisi masukan telah disediakan dengan peratus berat etanol yang berbeza-beza, iaitu 10 wt%, 30 wt%, 50 wt%, 70 wt% dan 90 wt% etanol. Suhu yang berlainan juga telah digunakan untuk menjalankan kajian, iaitu 30, 40, 50, 60 and 70 °C. Membran PVA zeolit tanah liat komposit telah disediakan dengan melarutkan 0.2 wt% serbuk zeolit tanah liat dan 5 wt% PVA ke dalam air suling yang berlainan. Larutan ini dikacau selama 24 jam dalam suhu bilik untuk menghasilkan larutan PVA zeolit tanah liat. Lapisan sokongan membran komposit pula disediakan melalui proses songsangan fasa menggunakan larutan tuangan yang mengandungi campuran 12 wt% polisulfon, 11 wt% metilselusof and 77 wt% N,N-dimetilformidamida (DMF). Membran komposit telah disediakan dengan menyalutkan larutan 1.0 wt% PVA zeolit tanah liat ke atas membran poros polisulfon. Membran tersebut telah digunakan untuk memisahkan campuran larutan ethanol-air melalui pervaporasi. Kesimpulannya, apabila kepekatan suapan dan suhu suapan meningkat, kememilihan membran meningkat dan kebolehresapan (fluks) menurun. Adalah didapati juga, membran PVA zeolit tanah liat yang telah

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dihasilkan bersifat padat, memilih air, mempunyai kekuatan mekanikal yang baik dan sesuai digunakan dalam proses pemisahan campuran etanol-air melalui pervaporasi.

1.0   INTRODUCTION

Recently, the separation of ethanol-water mixture by pervaporation techniques using zeolite membrane has been given much attention. For most industrial and fuel uses, the ethanol must be purified. Fractional distillation can concentrate ethanol to 96% volume; the mixture of 96% ethanol and 4% water is an azeotrope with a boiling point of 78.2 °C and cannot be further purified by distillation.
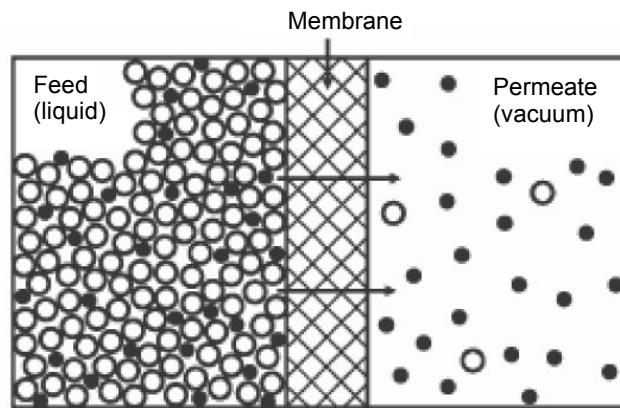
Figure 1.1   Diagram of pervaporation across a membrane [2]

Pervaporation is an energy efficient combination of membrane permeation and evaporation. It's considered an attractive alternative to other separation methods for a variety of processes. Pervaporation is a contraction of the terms of permeation and evaporation because the feed is a liquid, and vapor exits the membrane on the permeate side as shown by the diagram in Figure 1.1.

Pervaporation allows separations of some mixtures that are difficult to separate by distillation, extraction, and sorption. Pervaporation has advantages in separating azeotropes, close-boiling mixtures, and thermally sensitive compounds, and removing species present in low concentration. Only a fraction of a mixture is vaporized during pervaporation, and lower temperatures than those required in distillation are usually used. In addition, membranes operate continuously without requiring sorbent regeneration, and they are modular, which allows design flexibility. There are the reasons why membrane processes involving membranes economically attractive in many industrial applications.

Normally, the pervaporation process is separated into three steps:

(i)   Sorption of the permeable component into the separating layer of the membrane.
(ii) Diffusive transport of the substance across the membrane.
(iii) Desorption of the substance at the permeate side of the membrane.

This multistage process is evidently much more complex than a single vaporation step, and it is easily understandable that the composition of the pervaporation may widely differ from that of the mixed vapor evolved after the establishment of free liquid-vapor equilibrium. The use of an appropriate membrane generally makes it possible to separate a number of binary azeotropic mixtures [1].

Polyvinyl alcohol is a light, white, powdery solid when pure. PVA can be obtained in molecular weights from a few thousand up to about a million, the upper limit being largely defined through chain termination by acetaldehyde in the polymerization of vinyl acetate and by other impurities in other types of polymerization. PVA is one of the important membrane pervaporation materials for dehydration from organic solvents for its chemical stability, membrane-forming ability and heat-resistant properties. Besides the good, PVA has a poor stability in aqueous solution that needs to be in solubilized by crosslinking other modification in order to increase it's stabilize.

On the other hand, zeolites are inorganic crystalline structures that have uniform, molecular-sized pores. These inorganic structures have been used extensively as catalyst and absorbents. More recently, continuous polycrystalline zeolite layer have been deposited on porous supports and used as zeolite membranes. Suzuki reported that the first zeolite membranes in 1987. A zeolite membrane is a porous layer that can separate mixtures by adsorption and diffusion differences, and, in some cases, by molecular sieving. Some zeolite membranes' properties give zeolite membranes advantages over many polymeric membranes, which are zeolite membranes do not swell, they have uniform, molecular-sized pores that cause significant differences in transport rates for some molecules, and allow molecular sieving in some cases. Besides that, most zeolite structures are more chemically stable than polymeric membranes, allowing separations of strong solvents or low pH mixtures. Zeolites are also stable at high temperature (as high as 1270 K for some zeolites).

In developing new membranes and synthesis techniques, there are many application of zeolite membrane in separations, chemical sensors, and catalytic membrane reactor. In contrast, zeolite membranes have been used for pervaporation in laboratory studies, dehydrating alcohols and other organic compounds by pervaporation for solvent recovery. Furthermore, pervaporation through zeolite membranes has potential applications in removing organic compounds from water for water treatment and purification, in concentrating ethanol from fermentation broths for alternative fuel

production, and in separating isomers, such as xylenes or linear and branched alkanes if the fraction to be removed is small.

2.0   EXPERIMENTAL

2.1   Materials and Apparatus

Cyanex 272, Cyanex 302 and D2EHPA obtained from Fluka Company. All extractants were dissolved in kerosene as a diluent. All extractants and the diluent used are industrial grade and used as received. Nitric acid and sodium hydroxide solutions were used to adjust the initial pH of the photographic waste solutions. The photographic waste sample used was obtained from photographic shops. The photographic waste sample used was obtained from photographic shops. Since the photographic waste sample is very sensitive to temperature as well as light, it was therefore kept in a refrigerator to prevent any ageing effect or sedimentation of the sample constituents. Reagents for this experiment come from various resources. Powder of polyvinyl alcohol provided by Fluka, liquid Dimethyl formamide (DMF) provided by Labscan Asia Co. Ltd, solid polysulphone provided by Amoco, clay (kaolin) provided by Labscan Asia Co. Ltd, ethanol provided by Rinting Scientific supplier and methyl cellosolve/ethylene glycol provided by Krass. Whereas, for the apparatus that used in this study were scanning electron microscope (SEM) apparatus, SOLTEQ Pervaporation Bench Test Unit (Model: TR 12) and refractometer.

2.2   Preparation of 5 wt% PVA Solution

In order to prepared pure PVA solution, the powder of PVA was needed. For every 5 gram PVA powder that measured, 95 ml of distilled water as a solvent used to dissolve PVA powder. The result was non-clear solution. Then, the solution was stirred and heated. When the temperature reach 70 °C, rate of dissolved of PVA increased and the solution become clearer. Heating continued for about half of 1 hour to let the temperature reach until 97 – 98 °C. At this temperature, all of the PVA powder was dissolved. The solution that produced was a 5 wt% of PVA solution and then was filtering with pump filter to eliminate the non-dissolve powder and unwanted material.

2.3   Preparation of 5 wt% PVA Zeolite-clay Solution

In order to prepare PVA, zeolite-clay solution, the powder of zeolite-clay was required. For every 0.2 wt% of zeolite-clay powder that measured, and added in PVA solution to dissolve zeolite-clay powder, dispersed with the help of sonicator for 15 minutes and kept stirring for overnight. The result was non-clear solution. The solution that produced was a 5 wt% of PVA zeolite-clay solution which then filter with pump filter to eliminate the non-dissolve powder and unwanted material.

2.4 Preparation of Porous Support Layer

The porous support layer that used in this research is the polysulfone. The porous polysulfone solutions prepared via phase inverse process from a casting solution containing 12 wt% polysulfone, 11 wt% methyl cellosolve, and 77 wt% N,N-dimethylformamide (DMF). The solution stirred and heated below 50 °C until all of the powders dissolved. Next, the porous polysulfone solution casted onto a paper fabric held on a glass plate with the aid of a glass rod to adjust the appropriate thickness. The cast film immediately immersed into a gel bath consisting of 50 wt% dimethylformamide and 50 wt% distilled water at room temperature for 10 minutes. Lastly, the resulted porous membrane immersed with distilled water for 24 hours and drier in air at room temperature.

2.5 Preparation of PVA Zeolite-Clay Composite Membranes

The composite membrane prepare by coating 5 wt% PVA zeolite-clay solution poured onto the porous polysulfone membrane with the aid of the dropper and a glass rod adjusted to the appropriate thickness. The resulted membranes were dried in air at room temperature.

2.6 Pervaporation of Ethanol-Water Mixtures by Using PVA Zeolite-Clay

2.6.1 Membrane

The pervaporation apparatus used in this research is illustrated in Figure 2.1. Permeation of ethanol-water mixture carried out through the membrane by an ordinary pervaporation technique. Pervaporation experiments conducted in the stirred batch cell. The temperature controlled by circulating water from a thermostatic bath (VWR Scientific 1167) to a water jacket that surrounded the feed compartment. First of all, the pervaporation apparatus was setting and tested by run the machine using distilled water to remove unwanted material in the machine. Then, the feed composition was running up to free machine from distilled water.

The fed solution with determined composition of ethanol/water mixture was stored in the feed tank. A peril static pump was used to circulate the feed solution from the feed tank to the membrane cell. The circulation rate was kept high to minimize concentration polarization in the permeation cell and maximize mixing of solution in the feed tank.

Vacuum pump was applied to the permeate vapour to condense it in a cold trap using an ice and collected in the glass cold trap. The downstream pressure will keep below 0.07 bar controlled by a vacuum regulator and the experiments conducted at different composition of feed 10 wt%, 30 wt%, 50 wt%, 70 wt% and 90 wt% ethanol concentration and also at different temperatures 30, 40, 50, 60 and 70 °C.

The weight of permeates collected in the cold trap were measured using a digital electronic balance and the permeate composition analyzed by taking its refractometric index, nD. The membrane performances were characterized in terms of permeation flux and permeate concentration. The separation factor, which was derived from the feed and permeates concentration, was defined as Equation (2.1).

$$\alpha = (\,yi/yj\,)/(\,xi/xj\,) \tag{2.1}$$

On the meantime, the pervaporation separation index, PSI used to determine the overall pervaporation membrane factor and the formula was given by:

$$PSI = J\,(\alpha - 1) \tag{3.1}$$

2.7   Scanning Electron Microscope (SEM) Test

In order to observe the morphology structure of PVA zeolite-clay membranes, the samples of those membranes was prepared by freezing the dried the membrane samples in liquid nitrogen and breaking them to produce a cross section. The specimens were sputtered coated with gold prior for a period of not less than 4 hours to macroscopic observation. When the specimens were ready, they ware put into SEM apparatus for observation on surface view and cross section view of the PVA zeolite-clay composite membrane structures. This test held at Ibnu Sina Institution, Fakulti Kejuruteraan Kimia dan Sumber Asli, UTM, Skudai.

2.8   Refractometric Index, nD Test

The refractomeric index test was conducted in a way to get the standard refractometric index value for every concentration of ethanol-water mixture. Besides that, the refractomeric index for permeate also taken in a way to get the composition of ethanol and water in it. This test was conducted by using the refractometer.

3.0   RESULTS AND DISCUSSION

3.1   Morphology Structure of PVA Zeolite-Clay Membrane

From Figure 3.1, it shows that PVA zeolite-clay composite membrane consists of two layers. The first layer which is above layer is PVA zeolite-clay layer while the second layer is known as support layer is polysulfone layer. For PVA zeolite-clay layer, it shows that it structured is quit packed even after the 1000× magnifiers. The second layer known as support layer consist of porous structured. This can be proved that, we can see clearly the porous structure after 1000× magnifiers by using SEM test. The thickness of PVA zeolite-clay composite membrane can be measured from this structured and it thickness was 488 µm.
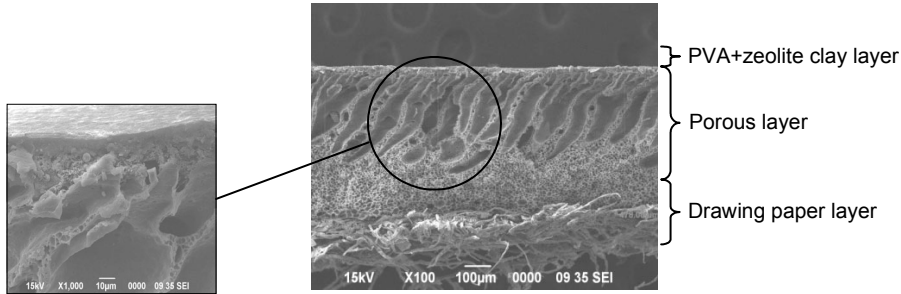
Figure 3.1 Morphological structure of PVA zeolite-clay composite membrane (after 100× and 1000× magnify)

3.2 Pervaporation Analysis

Pervaporation experiment was carried out by using "SOLTEQ Pervaporation Bench Test Unit (Model: TR 12)". The performance of pervaporation using PVA zeolite-clay membrane can be shows by the value of permeation flux, J_i and selectivity, α obtained. Solution of ethanol-water mixture is fed to the tank at five different ethanol concentrations that are 10 wt%, 30 wt%, 50 wt%, 70 wt% and 90 wt%; at five different temperatures that are at 30 °C, 40 °C, 50 °C, 60 °C and 70 °C. Table 3.1 and Table 3.2 showed all the data and results that obtained from pervaporation test.

3.2.1 Effect of Feed Concentration on Pervaporation of Ethanol-Water Mixture

Figure 3.1 and Figure 3.2 depicted permeate flux of water and total permeate flux as a function of varying feed composition. A substitution relation between permeate flux of water and total permeate flux are observed in these figures. Generally, theory obtained shows that permeate flux increases for increment of water composition in feed solution [3]. From these graphs, both showed that the results which had been
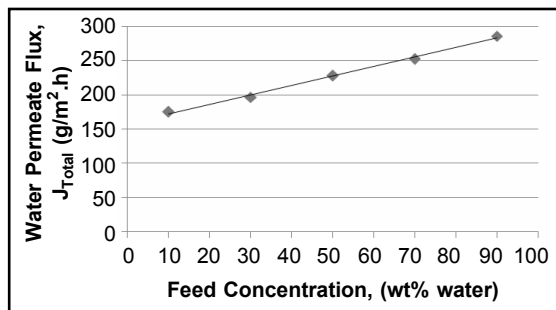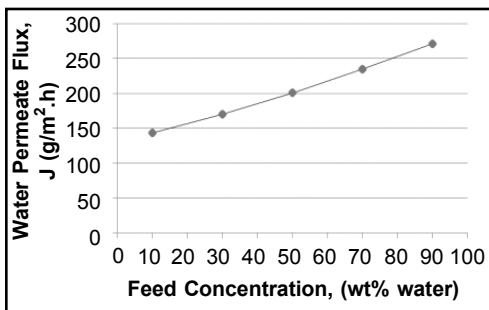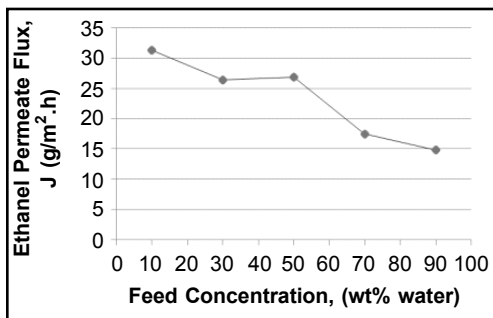

Figure 3.1 Effect of feed concentration on water permeate flux

Figure 3.2 Effect of feed concentration on total permeate flux

getting are obeying the theory. Both permeate flux are increasing linearly with water feed concentration.

This phenomenon may be due to plasticizing effect of water, and probable flow coupling between water and ethanol. As the water concentration in the feed increases, the amorphous regions of the membrane swell and the polymer chains become more flexible, allowing ethanol molecules also to pass through, thus lowering the ability of the membrane for selective transport [3].

Figure 3.3 showed that permeate flux of ethanol by varying feed composition. Generally, theory obtained shows that ethanol permeate flux decreases for increment of water composition in feed solution. From this graphs, it showed that the result obeys the theory. Ethanol permeate flux decreases with water feed concentration.

The characteristics of the sorption depended on the difference between the affinity of the components towards the polymer, the mutual interactions of the component, and the way the interactions with the polymer of each component affects the interactions of the other penetrates with the polymer. Generally, PVA zeolite- clay membrane which is hydrophilic membrane has a better affinity with water than ethanol. In addition to the strong interaction between ethanol and water, the smaller water molecules than ethanol molecules makes the diffusion of water easier than ethanol [3].


Figure 3.3   Effect of feed concentration on ethanol permeate flux
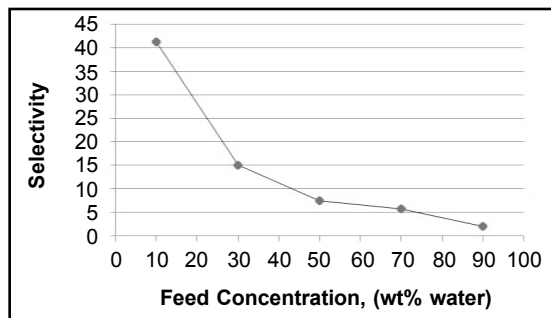
Figure 3.4   Effect of feed concentration on selectivity

Figure 3.4 showed the value of selectivity for different feed composition. Generally, theory obtained shows that selectivity decreases for increment of water composition in feed solution [4]. From this graphs, it showed that the result obeys the theory. Selectivity decreases with water feed concentration. This phenomenon can be explained in terms of the plasticizing effect of the water molecules. As the water concentration in the feed increases, the amorphous regions in a semicrystalline polymer become swollen and the polymer chains become more flexible, thus
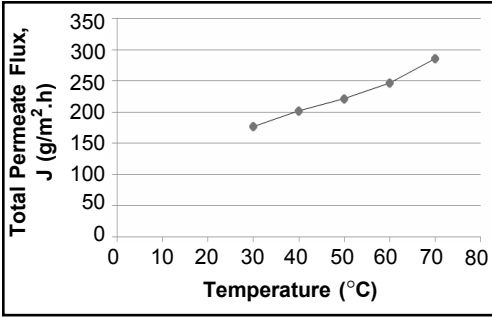
Figure 3.5   Effect of operating flux
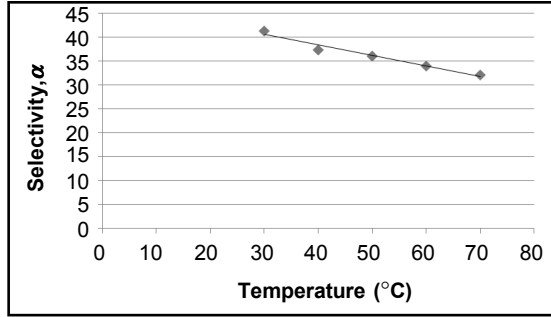
Figure 3.6   Effect of operating temperature on total temperature on selectivity

decreasing the energy required for flexible, thus decreasing the energy required for diffusive transport through the membrane. As the free volume due to the plasticizing effect of water molecules increases, the possibility of the permeation of interacted pairs as well as isolated molecules through the membrane becomes higher and the permeation rate of the molecules increases, leading to low membrane selectivity [4].

3.2.2   *Effect of Operating Temperature on Pervaporation of Ethanol-ater Mixture*

Temperature is an important process variable affecting the membrane performances in terms of pervaporation fluxes and selectivity. According to the theory, total flux increases with operating temperature and selectivity decreases when operating temperature increases. The graphs showed the effect of operating temperature on total permeation flux (Figure 3.5) and membrane selectivity (Figure 3.6).

Permeate flux is increased progressively with the increased in temperature which is obey the theory. As temperature increased, the thermal motion of polymer chains is intensified, creating more free volume in the polymer matrix, through which the permeating molecules of water and ethanol can diffuse. Therefore, the transport of both the permeating species is enhanced, leading to an increase in total permeation flux and decrease in selectivity. Dependence of the permeation flux on temperature can be related by an Arrhenius-type expression of the form:

$$J = A \exp (-E/RT) \tag{3.2}$$

where

   A = activation energy
   E = apparent activation energy for permeation
 T = absolute temperature
   R = gas constant

According to Eyring's theory, the thermal motion of a polymer chain in the amorphous regions randomly produces the "holes" through which the permeating molecules can diffuse. As the temperature increases, the frequency and amplitude of chain jumping increases and the resulting "holes" become larger, and the diffusion rate of individual permeating molecules and associated permeating molecules are high, so that the total flux increases with increasing the operating temperature [5].

During solution process, the interactions among permeates, such as water-water, ethanol-ethanol and ethanol-water might have an enhancing effect on the energy of solution. In contrast, the interactions of permeates with the membrane are thought to diminish the energy required for solution. Thus, the lower the temperature, the stronger the tendency for mutual association between permeates. Therefore, the solubility is lower. As the temperature increases, the interaction between permeates becomes weaker and the interaction between permeate and membrane is restored. Therefore, the solubility increases caused to decreasing of selectivity [6].

The individual permeation fluxes of the permeating species were calculated from total permeate rate and permeate composition. Figure 3.7 and 3.8 show the effect of temperature on permeate fluxes of water and ethanol respectively.
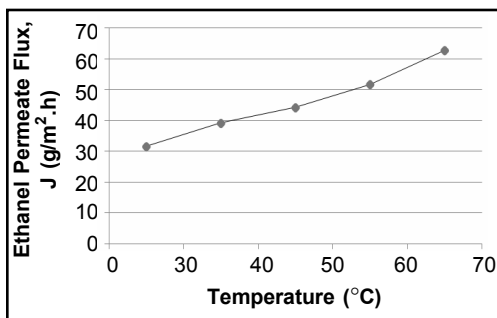
Figure 3.7   Effect of operating temperature on water permeate flux
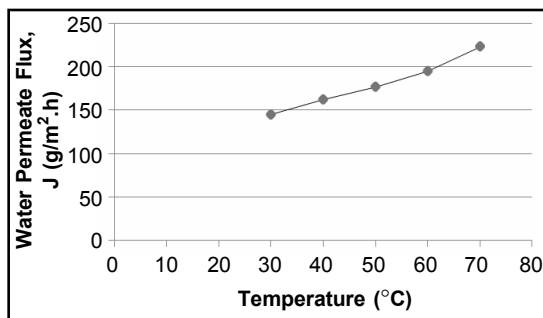
Figure 3.8   Effect of operating temperature on ethanol permeate flux

It can be seen that both water permeate rate and ethanol permeate rate increases as the temperature increases in the entire composition range. However, ethanol permeate flux showed lower value than water permeate flux for each temperature feed solution. This is because the activation energy for transport of water is lower than that of ethanol, indicating that water molecules required less energy than ethanol molecules to facilitate permeation through membrane. This difference in the activation energy for water and ethanol allow us to speculate that ethanol permeates by a random molecular diffusion within the amorphous matrix and water permeates by a selective transport through hydrophilic moiety in the polymer. The difference in the activation energy for each component may arise from several material factors such

as the molecular size and affinity between permeates and membrane. Consequently, water molecules are preferentially absorb and permeates more easily compared to ethanol because of it molecular size smaller and higher affinity for membrane [7].

4.0   CONCLUSION

Based on the results and discussions, it can be concluded that the separation performance of the membrane was affected by operation parameters, feed concentration and temperature. As the concentration of water in the feed increases, the flux is increases and decreases in selectivity. From this research, it is verified that as the temperature increases, flux will increase and selectivity will decreases.

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