

Chapter 4

Results and Discussion

4.1 Membrane Characterization

Chitosan is swellable in water and soluble in many dilute aqueous organic acids, crosslinking is the most effective method for improving membrane stability. In this study, sulfuric acid is chosen as the crosslinking agent since it is one of the most effective crosslinking agents for chitosan membranes (Semenova et al., 1997). The thickness of chitosan membranes obtained was in the range of 40-50 μm . Effects of preparation conditions on properties of chitosan membranes are discussed in the following sections.

4.1.1 Swelling ratio

The experimental results show that swelling ratio of uncrosslinked membrane was higher than that of crosslinked membranes. The swelling ratio of uncrosslinked membrane was 0.2317 while the swelling ratio of chitosan membranes crosslinked by sulfuric acid were in the range of 0.2040-0.2281. Chitosan membranes which are treated in aqueous solutions of sulfuric acid are formed of a large amount of ionic groups of $-\text{NH}_3^+$. These cationic amine groups in chitosan and sulfate ions have a coulombic interaction. Therefore, they crosslink chitosan main chains ionically, as shown in Figure 4.1, change intermolecular hydrogen bonding resulting in decrease of the crystalline region of chitosan which is in line with the research's results of Volkov et al. (1998) and Mukoma et al. (2004). Figure 4.2 indicates that swelling ratio of the membrane increases with increasing concentration of sulfuric acid at constant crosslinking time and membrane formation temperature. High concentrations of sulfuric acid enhance protonation of the $-\text{NH}_2$

groups resulting in intermolecular electrostatic repulsion of chitosan chains and chains separation. This result is attributed to the increase of free volume in the polymer chains as also reported by Hamdine et al. (2005).

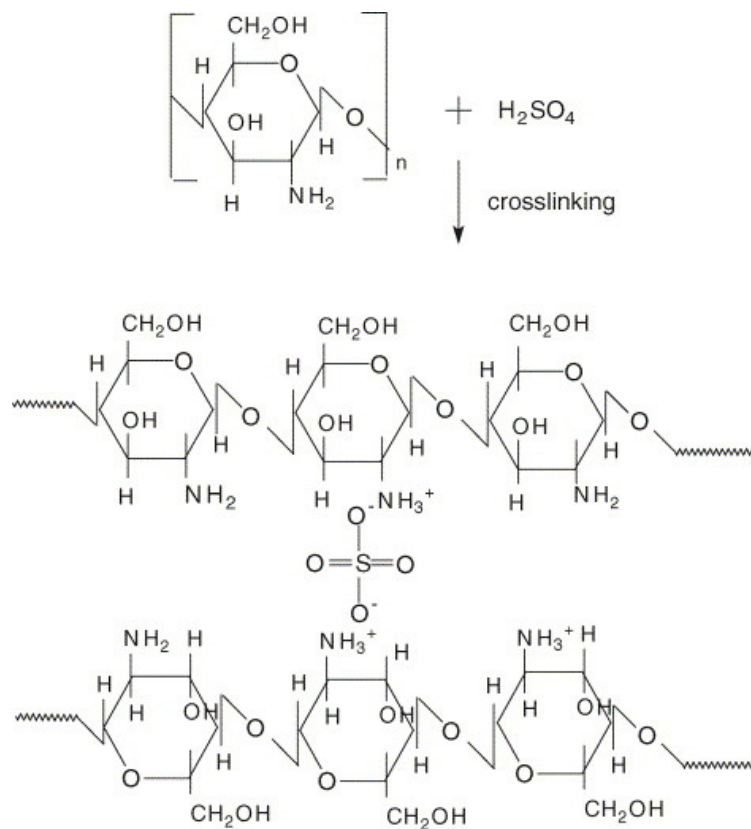


Figure 4.1 Chemical structures of ionic crosslinked chitosan membrane (Devi et al., 2006).

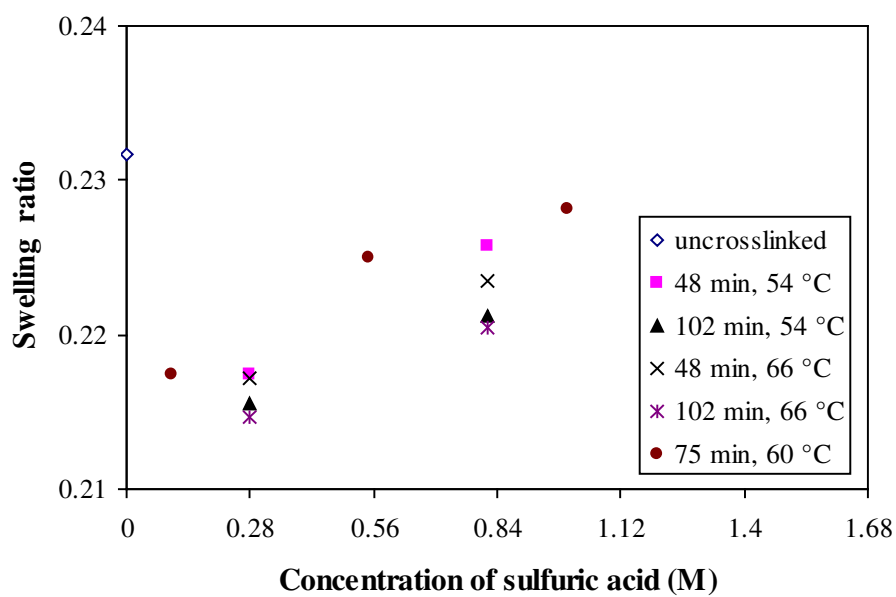


Figure 4.2 Effect of concentration of sulfuric acid on swelling ratio at different crosslinking times and membrane formation temperatures.

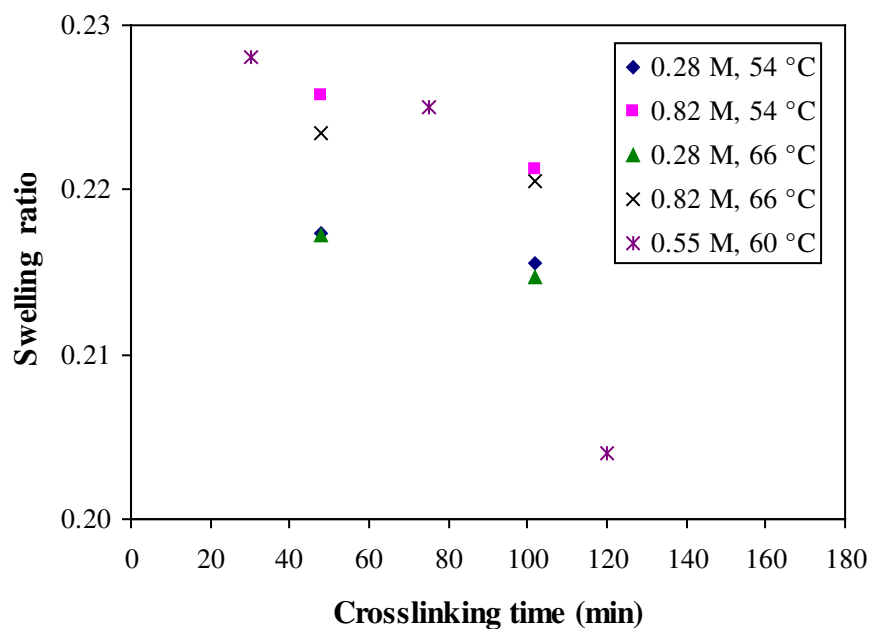


Figure 4.3 Effect of crosslinking time on swelling ratio at different concentrations of sulfuric acid and membrane formation temperatures.

The effect of crosslinking time on swelling ratio is shown in Figure 4.3. Swelling ratio decreases with increasing crosslinking time at constant concentration of sulfuric acid and membrane formation temperature because a coulombic interaction between protonated amino groups of chitosan and sulfate ions increase. This result is attributed to the decreasing of free volume in the polymer chains and the reducing of the mobility of polymer segments, leading to reductive swelling of the membrane which is in agree with the researchs of Nam and Lee (1999a), and Lee et al. (1997).

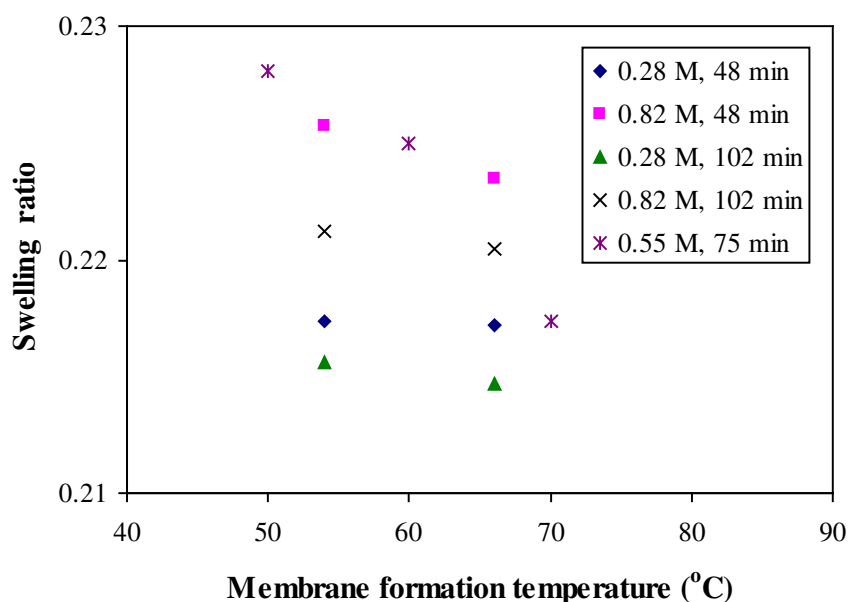


Figure 4.4 Effect of membrane formation temperature on swelling ratio at different concentrations of sulfuric acid and crosslinking times.

Figure 4.4 illustrates that swelling ratio decreases with increasing membrane formation temperature because during membrane formation at higher temperature polymer segments increase mobility. Thus, chitosan performs more crystallinity then the diameter of the diffusion channels decreases and packing density of membrane increases as also reported by Nam and Lee (1999b).

4.1.2 Tensile strength

Tensile strength increases by increasing concentration of sulfuric acid and crosslinking time at constant membrane formation temperature, as presented in Figure 4.5 and 4.6. Tensile strength of a uniform membrane depends on integrity of its structure. When the membrane is crosslinked more interchain as well as intrachain bonds are introduced into the structure, this in turn leads to an increase in compactness and subsequent increase in the tensile strength which is in line with the research's result of Thacharodi and Rao (1993).

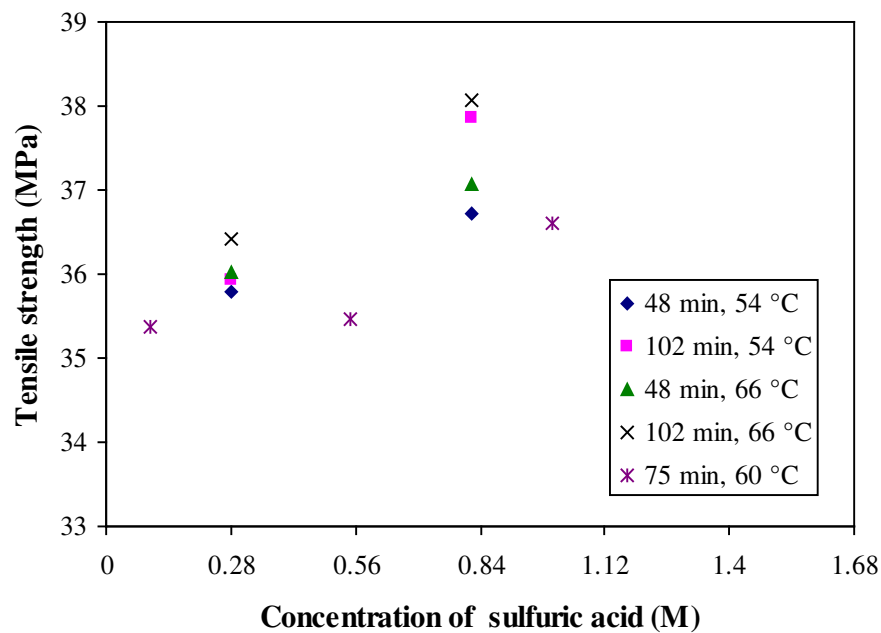


Figure 4.5 Effect of concentration of sulfuric acid on tensile strength at different crosslinking times and membrane formation temperatures.

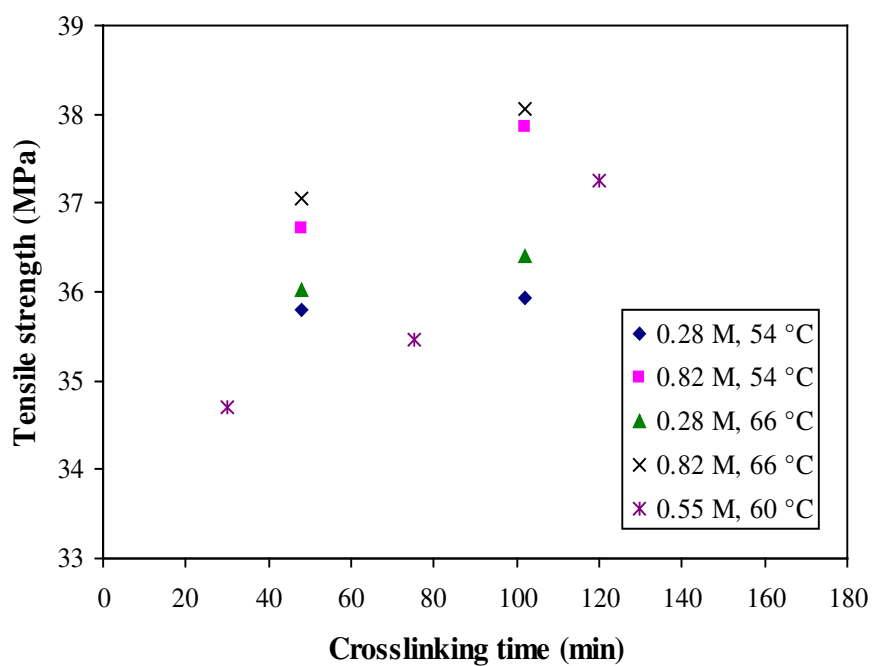


Figure 4.6 Effect of crosslinking time on tensile strength at different concentrations of sulfuric acid and membrane formation temperatures.

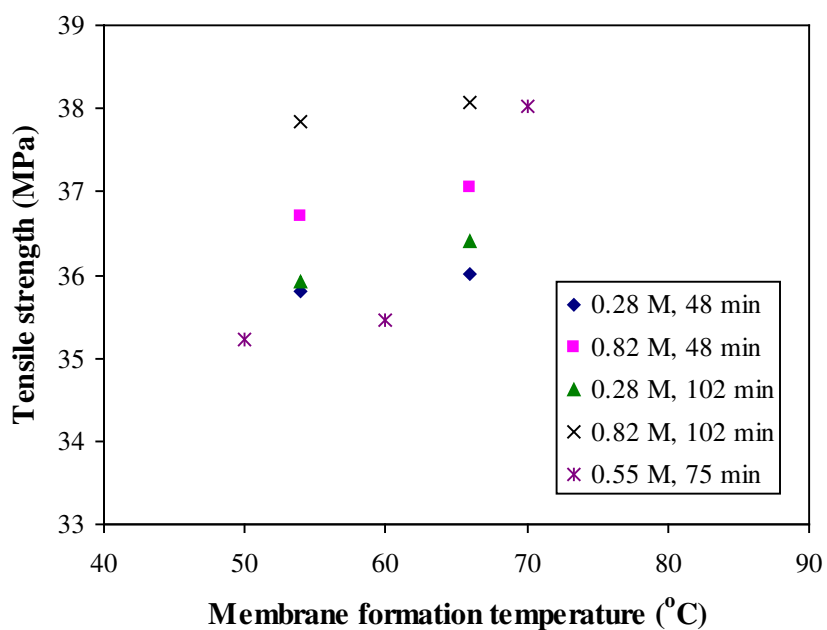


Figure 4.7 Effect of membrane formation temperature on tensile strength at different

concentrations of sulfuric acid and crosslinking times.

In Figure 4.7, tensile strength increase when membrane formation temperature increases since membrane structure obtained at higher membrane formation temperature contains more crystallinity.

4.1.3 Sorption selectivity

In Figure 4.8, the sorption selectivity of water decreases with increasing concentration of sulfuric acid at constant crosslinking time and membrane formation temperature. This result is attributed to the increase of free volume in the polymer chains. At high concentration of sulfuric acid, the excessively high water sorption, together with the increased flexibility of the polymer network, makes the membrane become much more swollen. Thus, ethanol can diffuse more easily into the membrane, resulting in a higher amount of sorbed ethanol.

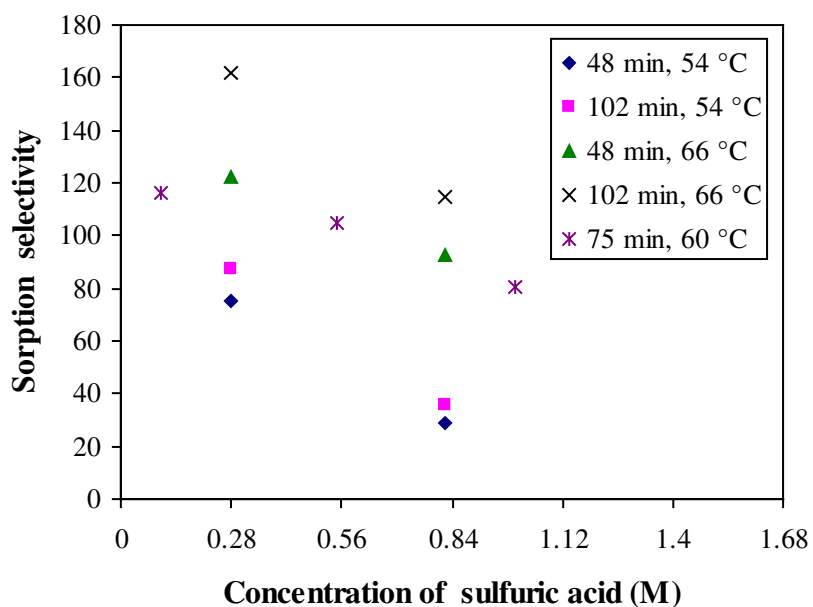


Figure 4.8 Effect of concentration of sulfuric acid on sorption selectivity of water at different crosslinking times and membrane formation temperatures.

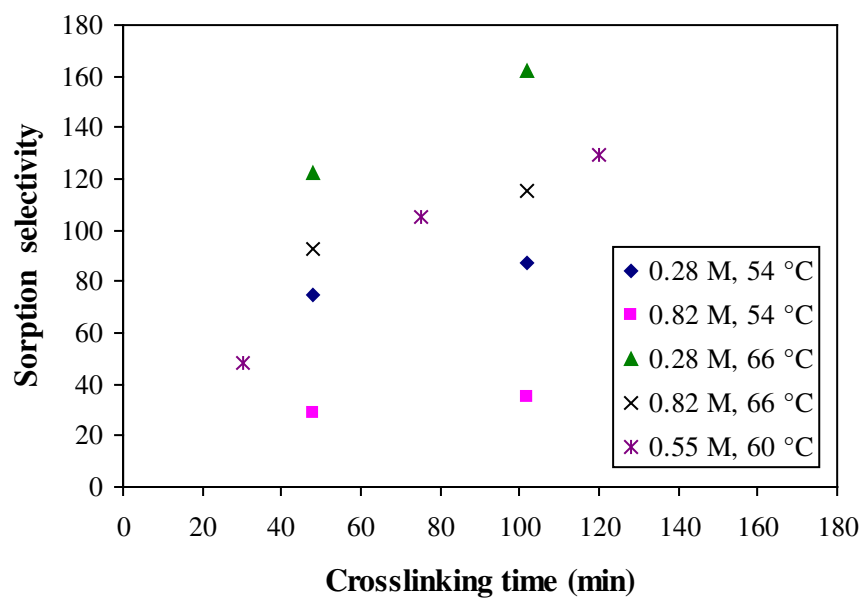


Figure 4.9 Effect of crosslinking time on sorption selectivity of water at different concentrations of sulfuric acid and membrane formation temperatures.

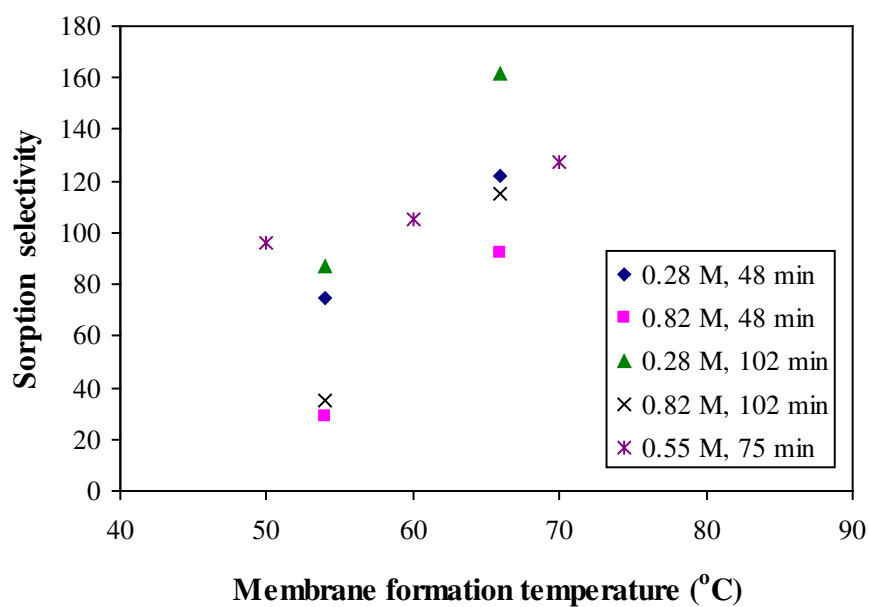


Figure 4.10 Effect of membrane formation temperature on sorption selectivity of water at different concentrations of sulfuric acid and crosslinking times.

In Figure 4.9, sorption selectivity increases with increasing crosslinking time because free volume of membrane decreases and the mobility of polymer segments reduces. So, water has the better affinity towards the membrane compared to ethanol because molecular size of water is smaller than that of ethanol as also reported by Volkov et al. (1998). In Figure 4.10, sorption selectivity increases with increasing membrane formation temperature since at higher temperature chitosan performs more induced crystallinity then the diameter of the diffusion channels decreases. Therefore, water which has better affinity towards the membrane compared to ethanol can be absorbed more.

4.1.4 Pervaporation performance

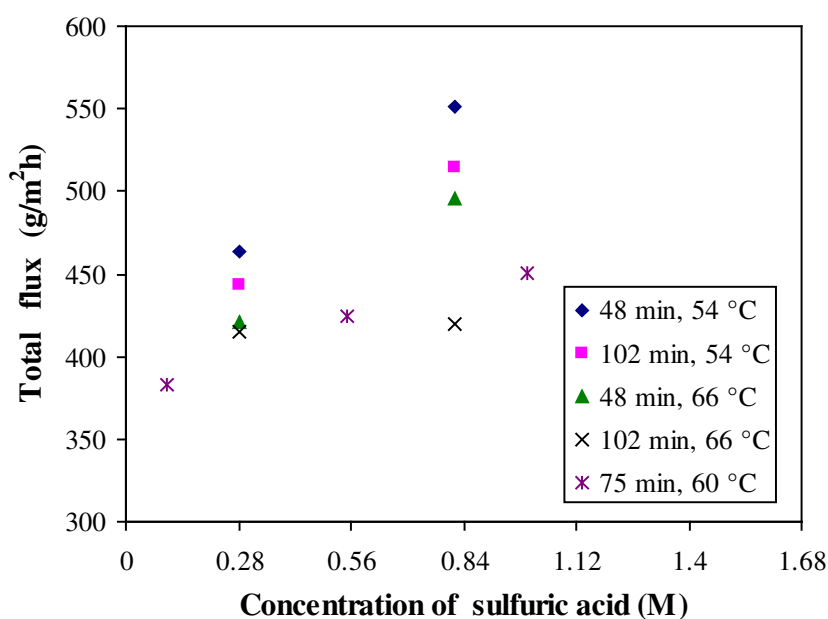


Figure 4.11 Effect of concentration of sulfuric acid on total flux for dehydration of 87 %w/w ethanol at 60 °C through membrane prepared at different crosslinking times and membrane formation temperatures.

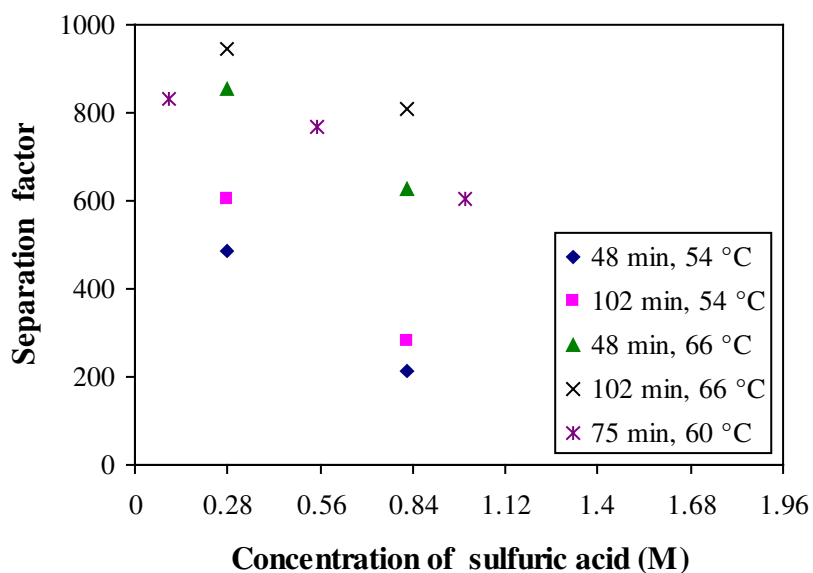


Figure 4.12 Effect of concentration of sulfuric acid on separation factor for dehydration of 87 %w/w ethanol at 60 °C through membrane prepared at different crosslinking times and membrane formation temperatures.

In Figure 4.11 and 4.12, the separation factor decreases, but total flux increases with increasing concentration of sulfuric acid at constant crosslinking time and membrane formation temperature. These are due to larger free volume in membrane structure which makes ethanol diffuse more easily through the membrane. Ethanol is normally difficult to diffuse into the non-swollen membrane due to its large molecular size.

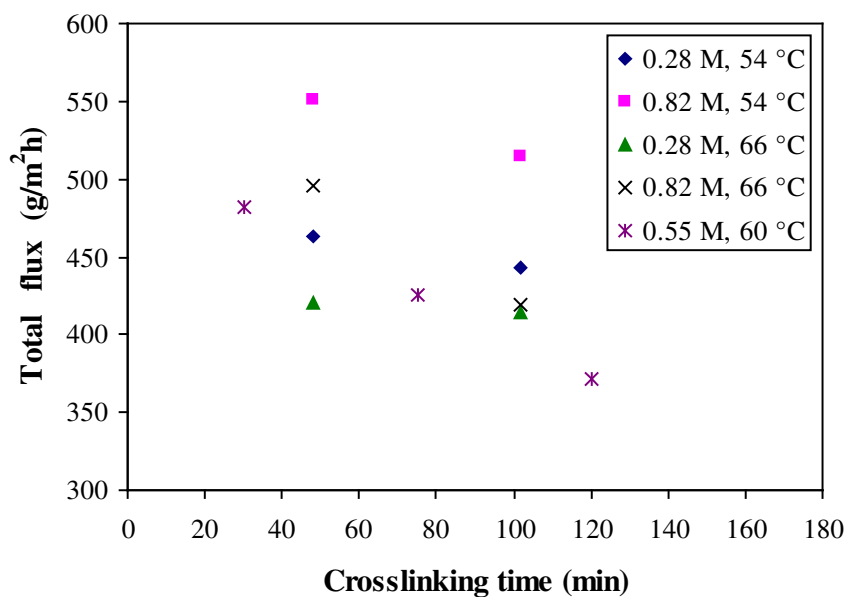


Figure 4.13 Effect of crosslinking time on total flux for dehydration of 87 %w/w ethanol at 60 °C through membrane prepared at different concentrations of sulfuric acid and membrane formation temperatures.

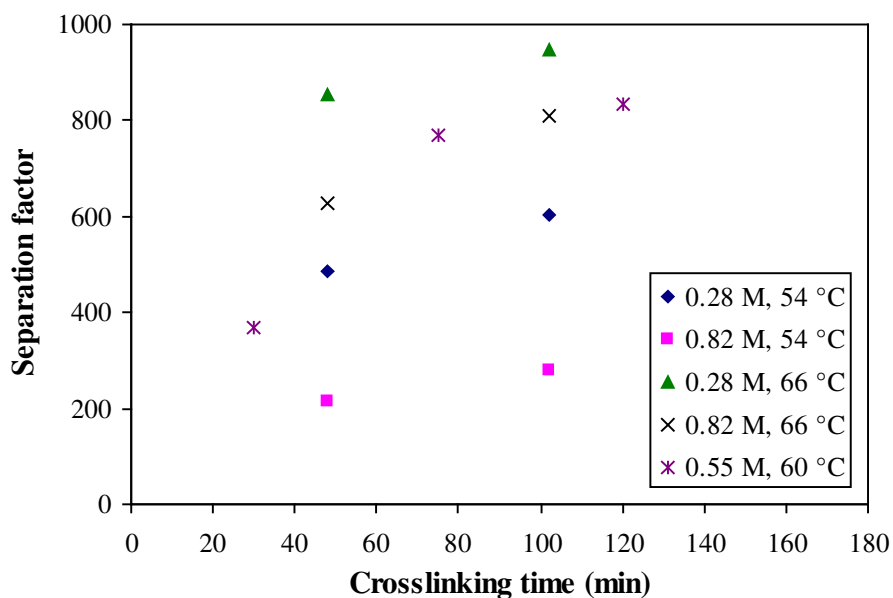


Figure 4.14 Effect of crosslinking time on separation factor for dehydration of 87 %w/w ethanol at 60 °C through membrane prepared at different concentrations of sulfuric acid and membrane formation temperatures.

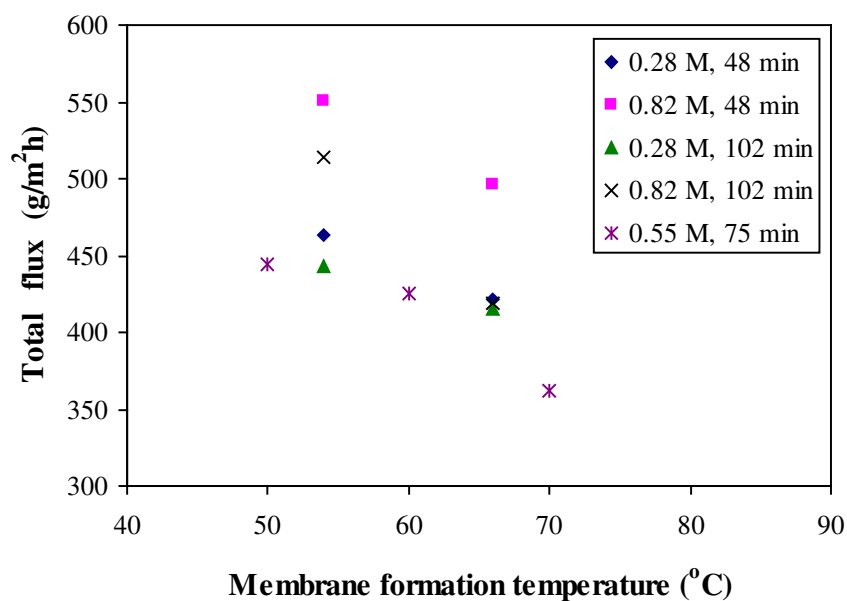


Figure 4.15 Effect of membrane formation temperature on total flux for dehydration of 87 %w/w ethanol at 60 °C through membrane prepared at different concentrations of sulfuric acid and crosslinking times.

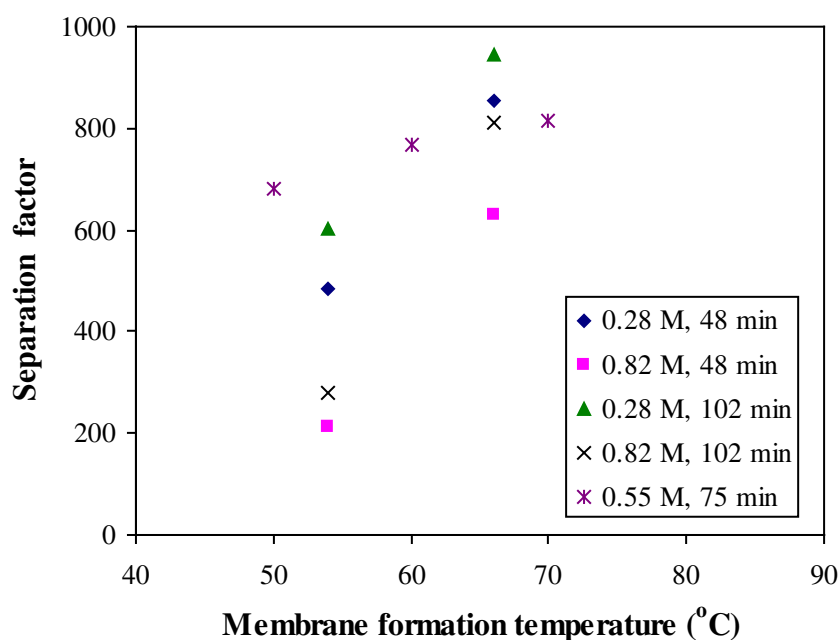
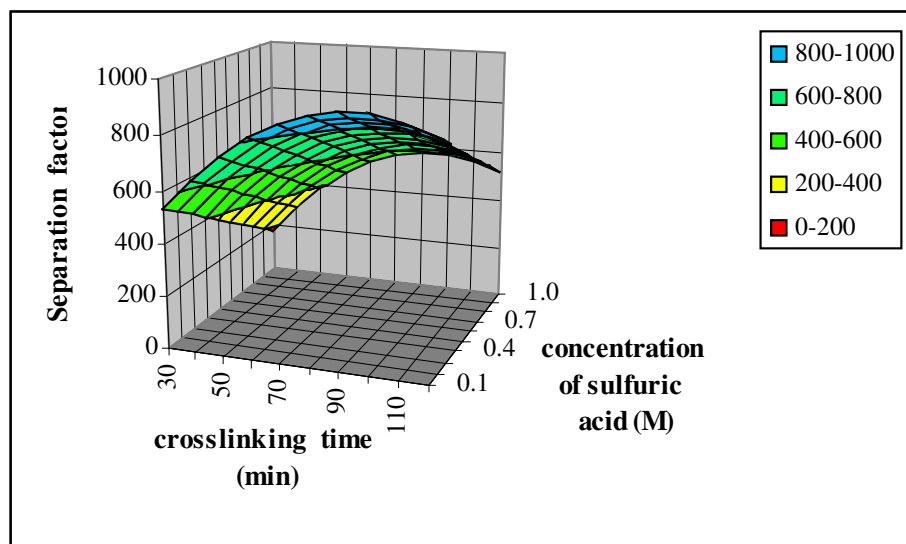
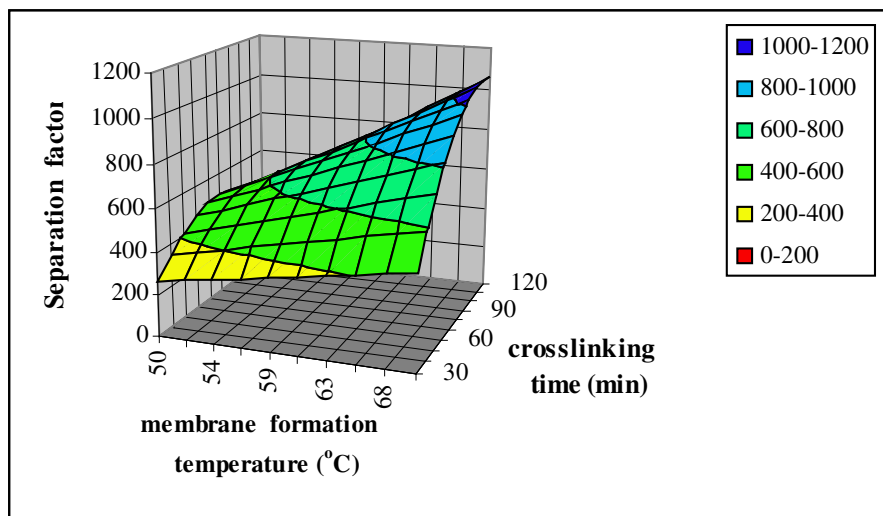


Figure 4.16 Effect of membrane formation temperature on separation factor for dehydration of 87 %w/w ethanol at 60 °C through membrane prepared at different concentrations of sulfuric acid and crosslinking times.

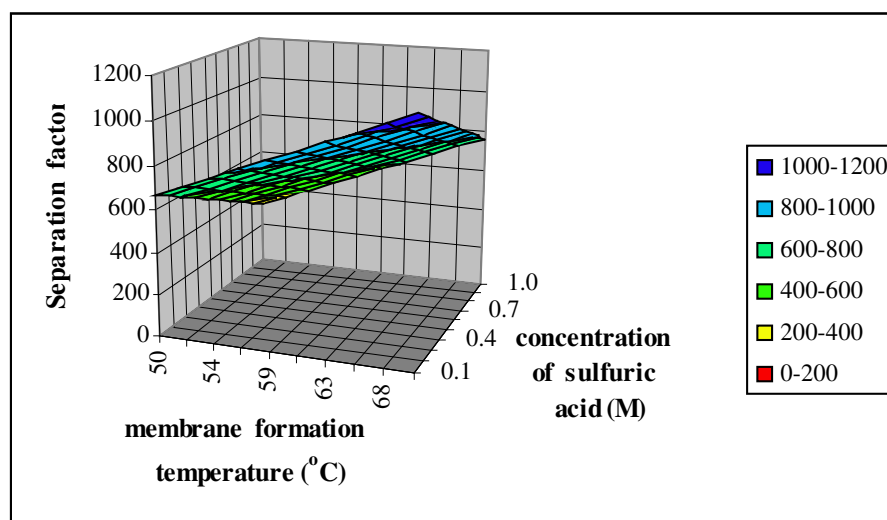
Figure 4.13 and 4.14 show effect of crosslinking time on pervaporation performance of water-ethanol mixture through chitosan membranes. By increasing the crosslinking time the degree of crosslinking increases, the membrane showed an increasing separation factor and decreasing total flux. Crosslinking packs the chitosan chains, decrease the free volumes in the membrane, and then deforms the crystalline region of chitosan chains (Lee et al., 1997). Mochizuki et al. (1989) studied the permselectivity of chitosan membranes crosslinked with HCl, CoSO_4 and H_2SO_4 , and suggested that ionic crosslinking is stronger than the coordination bond in chitosan. In Figure 4.15 and 4.16, separation factor increases, while total flux decreases with increasing membrane formation temperature because at higher membrane formation temperature chitosan induced more crystallinity. Therefore, it decreases diameter of the diffusion channels, resulting in water can better pass through the membrane compared to ethanol which is similar to the result of Ge et al. (2000).



(a)

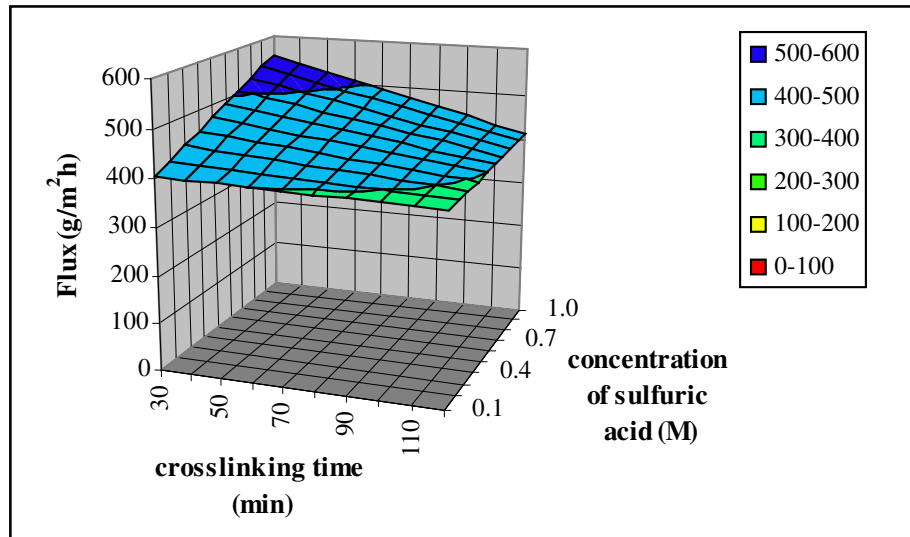


(b)

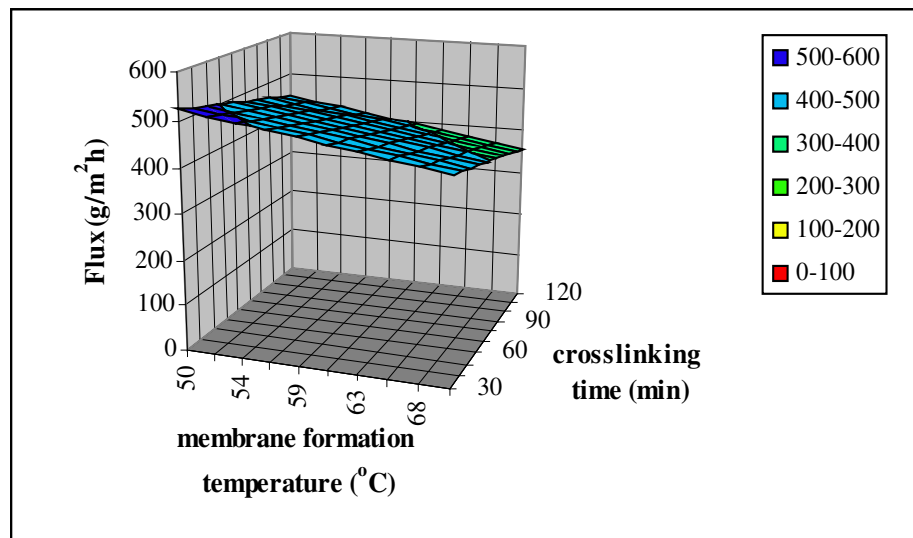


(c)

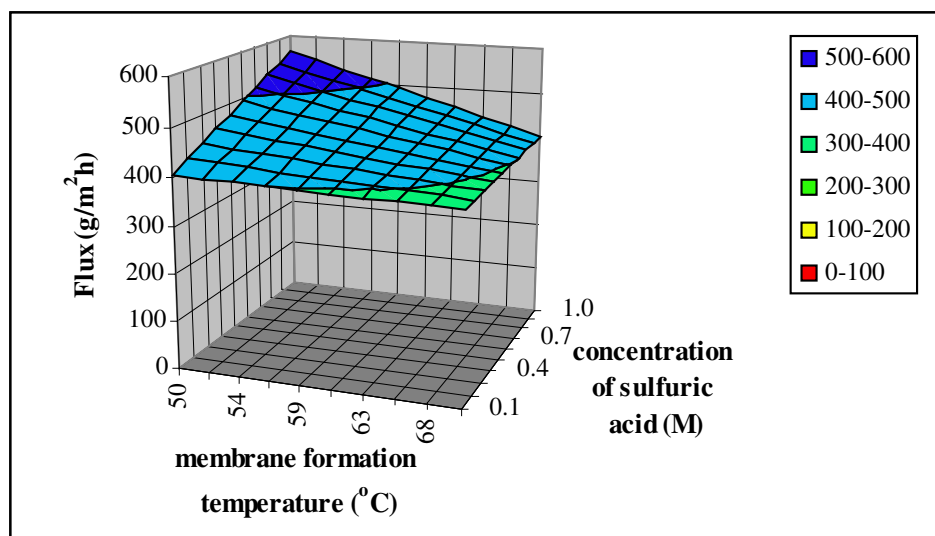
Figure 4.17 Effect of (a) concentration of sulfuric acid and crosslinking time, (b) crosslinking time and heating temperature, and (c) concentration of sulfuric acid and heating temperature, on separation factor for dehydration of 87 %w/w ethanol at 60 °C.



(a)



(b)



(c)

Figure 4.18 Effect of (a) concentration of sulfuric acid and crosslinking time, (b) crosslinking time and heating temperature, and (c) concentration of sulfuric acid and heating temperature, on flux for dehydration of 87 %w/w ethanol at 60 °C.

The results suggest that the membrane preparation conditions significantly affect separation factor and total flux, while slightly affect the swelling ratio, tensile strength and sorption selectivity of water. Thus, for choosing membrane preparation conditions in order to obtain optimum pervaporation performance, the effects on separation factor and total flux were considered. Results from using RSM investigated the membrane preparation conditions are presented in Figure 4.17 and 4.18. The optimum values of total flux and separation factor were in the range of 300-500 and 800-1000, respectively. The chitosan membrane formed at 66 °C and crosslinked with 0.28 M sulfuric acid for 102 minute gave the highest separation index of 399066, separation factor of 963 and total flux of 415 $\text{g/m}^2\text{h}$. Therefore, it was selected for further study for dehydration of ethanol.

4.2 Pervaporation studies

Performance of pervaporation is dependent not only upon the membrane but also upon the operating parameters such as feed concentration and feed temperature. Effects of operating parameters on pervaporation performance are discussed in the following sections.

4.2.1 Feed concentration

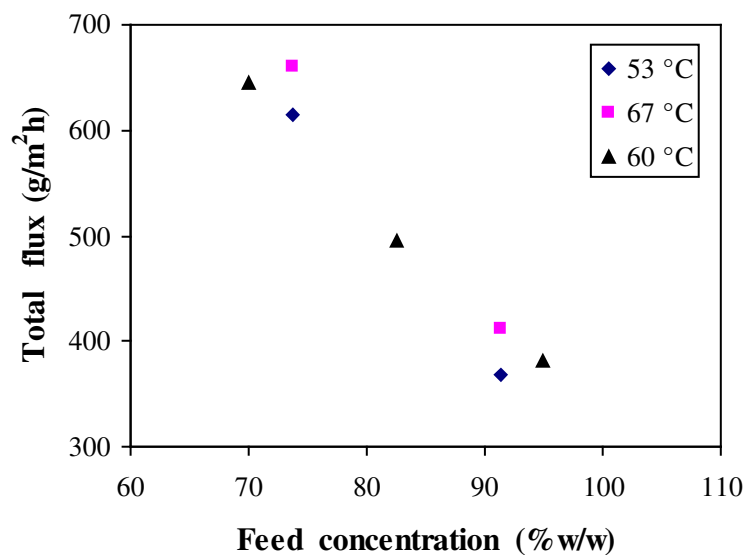


Figure 4.19 Effect of feed concentration on total flux for dehydration of ethanol at downstream pressure of 2.54 mm of Hg and different feed temperatures.

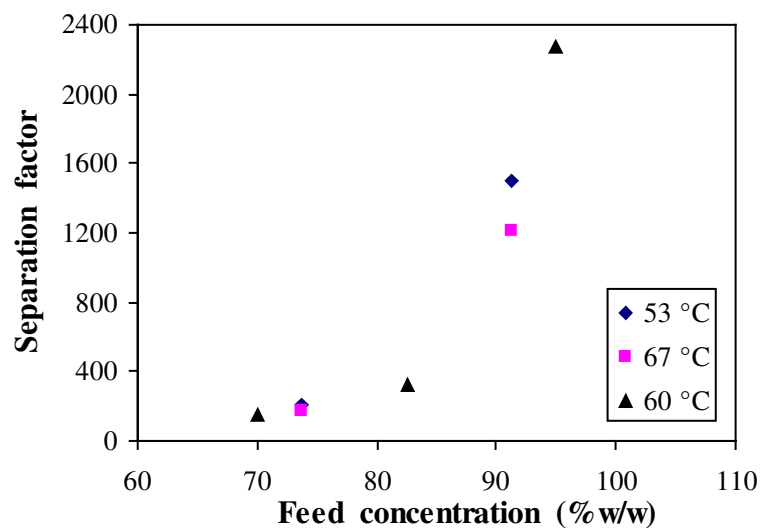


Figure 4.20 Effect of feed concentration on separation factor for dehydration of ethanol at downstream pressure 2.54 mm of Hg and different feed temperatures.

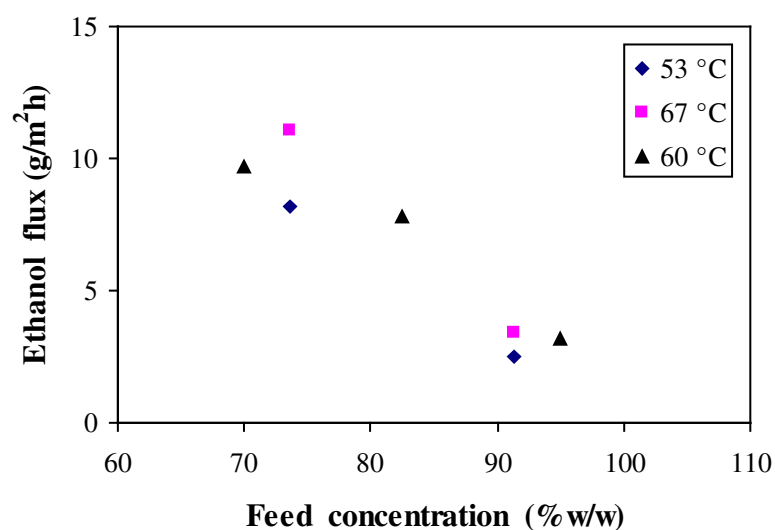


Figure 4.21 Effect of feed concentration on ethanol flux for dehydration of ethanol at downstream pressure 2.54 mm of Hg and different feed temperatures.

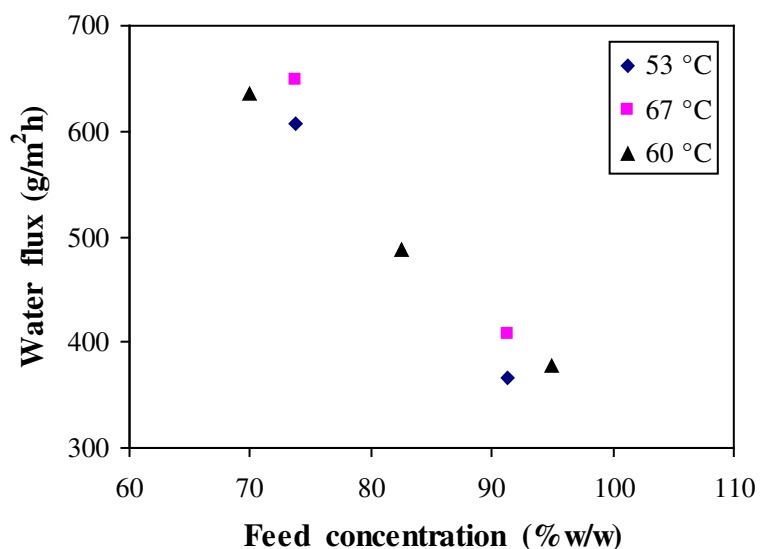


Figure 4.22 Effect of feed concentration on water flux for dehydration of ethanol at downstream pressure 2.54 mm of Hg and different feed temperatures.

The influence of feed concentration on pervaporation process was studied. The feed concentration was varied from 70 – 95 %w/w ethanol solution. In Figure 4.19 and 4.20, total flux decreases, while separation factor increases with an increasing in feed concentration. At higher water concentration in the feed, a strong interaction between water and membrane occurs which makes the membrane becomes much more swollen. Thus, free volume in polymer chains increases which makes ethanol diffuse more easily into the membrane. Therefore, in Figure 4.21 and 4.22, flux of both water and ethanol increases at higher water content in the feed. These results are similar to the works of Jiratananon et al. (2002) and Smitha et al. (2006).

4.2.2 Feed temperature

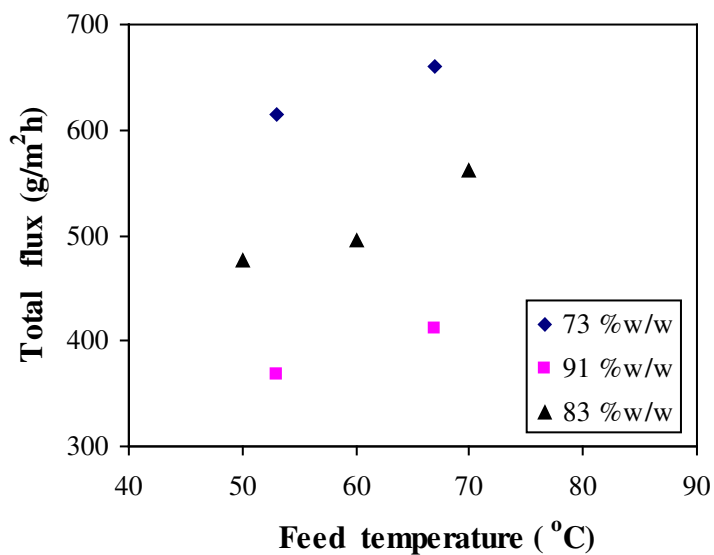


Figure 4.23 Effect of feed temperature on total flux for dehydration of ethanol at downstream pressure 2.54 mm of Hg and different feed concentrations.

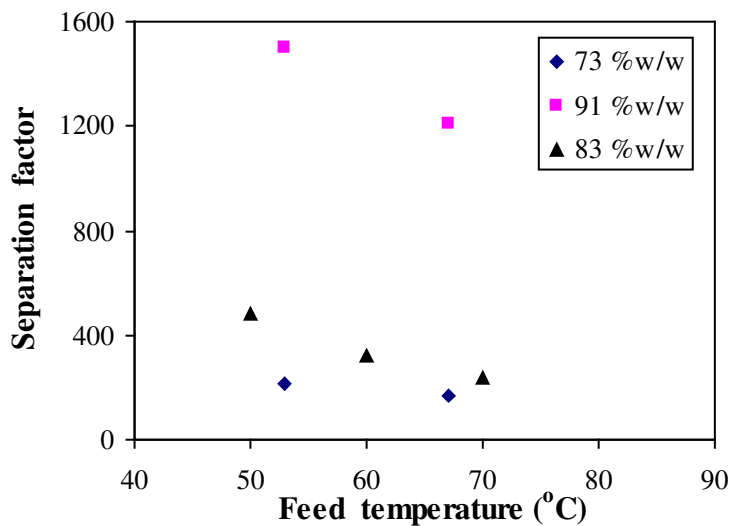


Figure 4.24 Effect of feed temperature on separation factor for dehydration of ethanol at downstream pressure 2.54 mm of Hg and different feed concentrations.

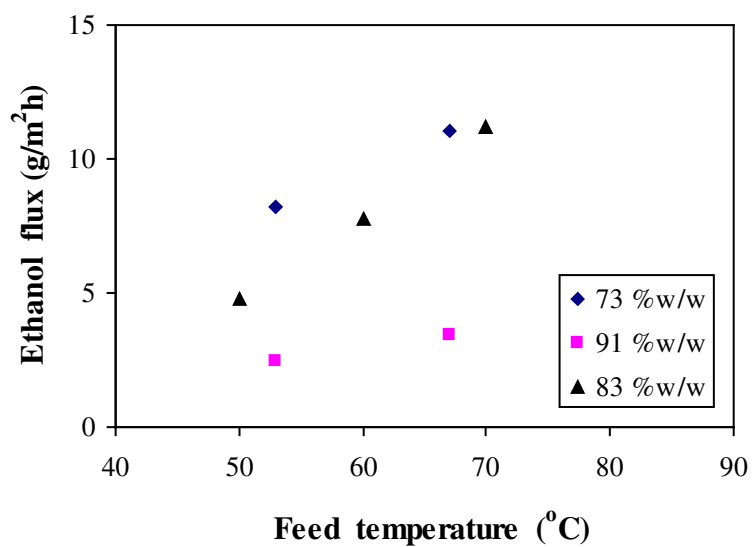


Figure 4.25 Effect of feed temperature on ethanol flux for dehydration of ethanol at downstream pressure 2.54 mm of Hg and different feed concentrations.

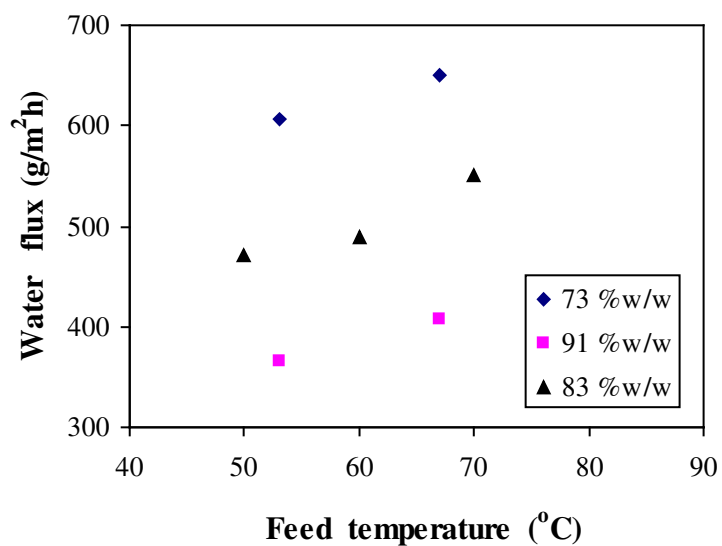


Figure 4.26 Effect of feed temperature on water flux for dehydration of ethanol at downstream pressure 2.54 mm of Hg and different feed concentrations.

It can be seen from Figure 4.23 and 4.24 that total flux increases, although separation factor decreases with increasing feed temperature since the plasticizing action of the permeates increases. Therefore, the permeation of diffusing molecules and associated molecules through the membranes becomes easier (Kittur et al., 2005). The decrease of separation factor was due to the increase of molecular motion and the increase in total flux may ensure from increasing free volume of polymer segments and polymer chain become much more swollen. Therefore, in Figure 4.25 and 4.26, flux of both water and ethanol increases at higher feed temperature which is in line with the result of Jiratananon et al. (2002).

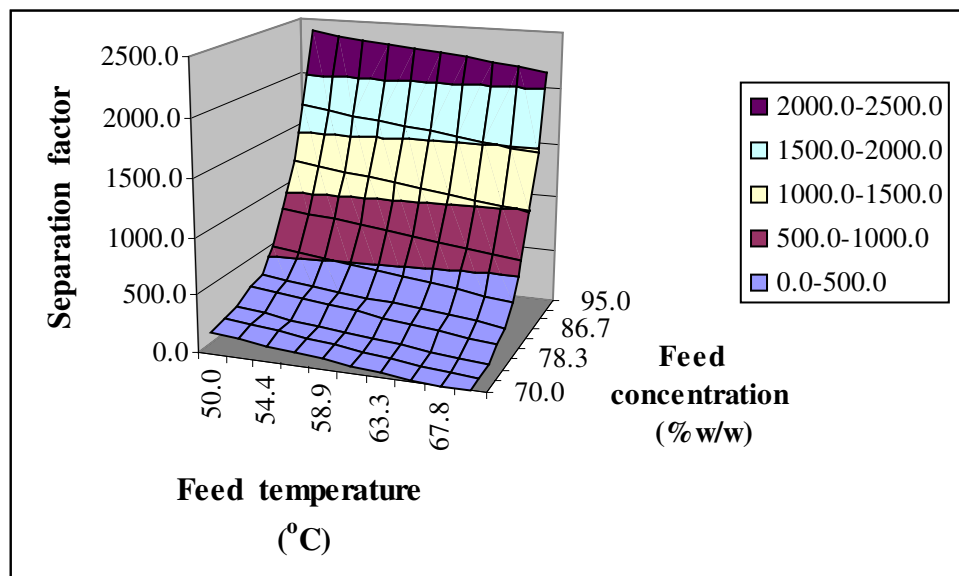


Figure 4.27 Effect of feed concentration and feed temperature on separation factor for dehydration of ethanol at downstream pressure 2.54 mm of Hg.

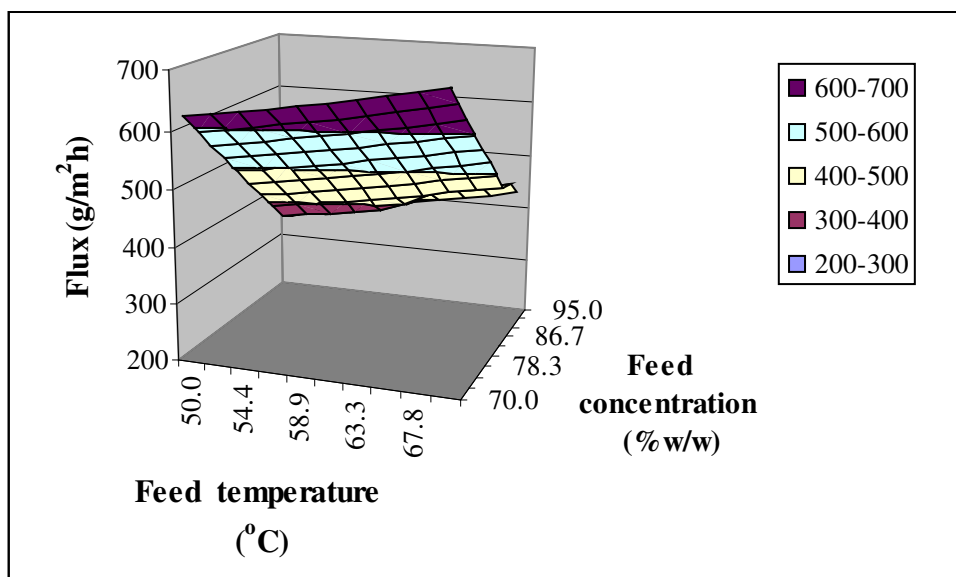


Figure 4.28 Effect of feed concentration and feed temperature on flux for dehydration of ethanol at downstream pressure 2.54 mm of Hg.

Results from using RSM investigated pervaporation performance are presented in Figure 4.27 and 4.28. The optimum values of total flux and separation factor were in the range of 300-700 and 1000-2500, respectively. The pervaporation operated at 70 °C and 95 %w/w ethanol gave the highest separation index of 918197, separation factor of 2146 and total flux of 428 g/m²h.

Table 4.1 Comparison of pervaporation dehydration of ethanol using various membranes

Membrane	EtOH concentration (%w/w)	Temperature (°C)	Total flux (g/m ² h)	Separation factor
CS-PES composite (Lee et al., 1997)	95	80	350	500
CS-sodium alginate (Kanti et al., 2004)	95	-	55	436.3

Table 4.1 Comparison of pervaporation dehydration of ethanol using various membranes (continued)

Membrane	EtOH concentration (%w/w)	Temperature (°C)	Total flux (g/m ² h)	Separation factor
CS/HEC-CA composite (Jiratananon et al., 2002)	95	60	220	16606
CS/PAAc (Nam and Lee, 1997)	95	80	22	19000
Novel two-ply composite (Moon et al., 1999)	95	60	70	1110
CS/N-methylol nylon 6 (Shieh and Huang, 1998)	95	60	350	560
Alginate/CS-PVDF (Huang et al., 2000)	95	50	95	202
CS dense (this work)	95	70	428	2145