CHAPTER IV

RESULTS AND DISCUSSION

In this study, the amount of a permeate sample was determined by a mass balance method presented in Appendix B.

The effect of the operating parameters, i.e. feed concentration, downstream pressure, feed temperature, and feed flow rate, on the flux and selectivity in pervaporation of methanol-water mixture using the PTFE/PP membrane were studied and the following results were obtained.

4.1 Effect of feed concentration

The permeate concentration, fluxes and selectivity were determined at using six different concentrations of methanol in feed (10 to 60 wt % methanol). All experiments in this section were carried out at temperature of 30 ^{o}C, downstream pressure of 34 cmHg, and feed flow rate of 17 ml min^{-1}. The fluxes and selection factors for methanol and water at various feed concentrations are shown in Table C.1 (Appendix C).

Figure 4.1.1 shows the methanol mass fraction in the permeate as a function of the methanol mass fraction in the feed mixture. It showed that pervaporation through the membrane ensures water enrichment in feed by preferential methanol transfer. The permeate concentration was found to linearly increase with an increase in the feed concentration.

Figure 4.1.2 shows the fluxes as a function of methanol mass fraction in the feed mixture. The total flux and methanol flux increased with an increase in the methanol content in feed. This is consistent with previous work [23, 34, 36, 38]. This may be due to the increasing probability of the methanol molecules contacting with the membrane. Then, the chemical interaction between the membrane and methanol is stronger than that between the membrane and water. Therefore, when the methanol content in feed increases, the interaction between the membrane and methanol becomes more significant, and the methanol sorption and diffusion capacity is enhanced. Using 10 to 60 wt % methanol, the total flux enhanced from 3.18 to 12.64 kg m^{-2} h^{-1} and the methanol flux enhanced from 0.75 to 8.82 kg m^{-2} h^{-1}. The water flux showed a minor change with an increase in the concentration of methanol in feed. Therefore, the water flux was only slightly affected by concentration of methanol in feed change.

Figure 4.1.3 shows the selection factor and PSI as a function of the methanol mass fraction in the feed. The effect of feed concentration on selection factor showed the behavior as same as on PSI. The selection factor and PSI rapidly decreased in the range of low feed concentration, up to 30 wt % methanol, and the level off to approximately of 1.5 and 9 kg m^{-2} h^{-1}, respectively, at feed concentration above 40 wt % methanol. Previous work reported that the selection factor decreased with an increase in the feed concentration [36, 38, 40]. At high methanol content in feed, high sorption of the permeants causes loosening of the polymer and easing diffusion of both the permeants. Hence, permeation selectivity decreases at high methanol content in feed. Figure 4.1.3 shows high values of selection factor and PSI at low concentration of methanol indicates that good pervaporation performance was obtained at low concentration of methanol. It is known that pervaporation is especially attractive when the concentration of the removed component is relatively low.

Feed concentration of 10 to 60 wt % methanol gave the total flux of 3.18 to 12.64 kg m^{-2} h^{-1}, the methanol flux of 0.75 to 8.82 kg m^{-2} h^{-1}, the water flux of 2.43 to 3.82 kg m^{-2} h^{-1}, the selection factor of 1.51 to 3.70, and PSI of 6.45 to 8.59 kg $m^{-2}h^{-1}$.

4.2 Effect of downstream pressure

The permeate concentration, fluxes and selectivity were determined at three different values of downstream pressure (12, 20, and 34 cmHg). All experiments in this section were carried out at temperature of 30 °C, and feed flow rate of 17 ml min^{-1} at six different concentrations of methanol in feed (10 to 60 wt % methanol). The fluxes and selection factors for methanol and water at various values of downstream pressure are shown in Table C.15 (Appendix C).

Figure 4.2.1 shows the methanol mass fraction in the permeate as a function of the downstream pressure. At each feed concentration, permeate concentration was found to increase with an increase in the downstream pressure. Therefore, the permeate concentration changes in the same direction with downstream pressure. The concentration of methanol in the permeate was found to be 23 wt % when 10 wt % methanol in feed and the downstream pressure of 34 cmHg were used.

Figure 4.2.2 shows the effect of the downstream pressure on fluxes. At all feed concentrations, the fluxes decrease with an increase in the downstream pressure. This is consistent with previous work [23, 39, 41, 44]. Since, there is a reduction of driving force for mass transport of components. The high methanol flux was obtained at high concentration of methanol and low downstream pressure The similar trend was found for the effect of downstream pressure on the water flux. At low methanol concentration, the downstream pressure had less effect on methanol flux and water flux. At downstream pressure of 12 cmHg, when the concentration of methanol in feed increased, the water flux increased, while the concentration of methanol in feed did not affect the water flux at downstream pressure of 34 cmHg.

Figure 4.2.3 shows the effect of the downstream pressure on the selection factor and PSI. The selection factor increased with an increase in the downstream pressure. The same behavior was obtained in previous work related to the separation of VOCs in aqueous solution using PTFE membrane [39]. This may be due to a reduction of the driving force to transport across the membrane and a decrease of membrane swelling. The selection factors at various concentrations and downstream pressure of 12 cmHg were found to be equal to 1, therefore, this pressure gave low efficiency on pervaporation performance. At low concentration of methanol in feed, the downstream pressure was very significant. For feed concentration of 10 wt % methanol, when the downstream pressure increased from 12 to 34 cmHg, the selection factor enhanced from about 1 to 4. At downstream pressure of 12 cmHg, PSI was found to increase with an increase in the concentration of methanol in feed and low values of PSI were obtained. When the downstream pressure increased from 20 to 34 cmHg, the PSI value decreased, the opposite trend with selectivity. It can be concluded that at low methanol content in feed, PSI value is significantly influenced by downstream pressure.

The suitable pervaporation performance of the membrane was obtained at high downstream pressure (34 cmHg), especially at low methanol content in feed.

4.3 Effect of feed temperature

The influence of feed temperature on pervaporation performance was determined at three different temperatures (30, 40, and 50 °C). All experiments in this section were carried out at downstream pressure of 34 cmHg, and feed flow rate of 17 ml min^{-1} at six different concentrations of methanol in feed (10 to 60 wt % methanol). The fluxes and selection factors for methanol and water at various feed temperatures are shown in Table C.16 (Appendix C).

Figure 4.3.1 shows the methanol mass fraction in the permeate as a function of the feed flow rate. All feed concentrations, permeate concentration decreased with an increase in the feed temperature. At the constant feed concentration, high temperature gave low permeate concentration.

Figure 4.3.2 shows the effect of feed temperature on fluxes. At each concentration of methanol in feed, insignificant difference in the total flux and the methanol flux are found at feed temperatures of 30 to 50 °C. Therefore, the feed temperature does not affect the total flux and the methanol flux. All feed concentrations, low values of water flux were obtained at feed temperature of 30 °C. At feed temperature of 40 to 50 °C, the water flux was only slightly affected by feed temperature change.

Figure 4.3.3 shows the effect of the downstream pressure on the selection factor and PSI. The selection factor and PSI were found to decrease with an increase in the feed temperature, in agreement with previous work [34, 38, 42, 43, 45]. The selection factor of 3.70 and PSI of 8.59 kg m^{-2} h^{-1}, which are the higher values, at feed concentration of 10 wt % methanol and temperature of 30 °C.

According to the free volume theory, the thermal motion of polymer chains produces free volume. As temperature rises, the frequency and amplitude of chain jumping increase and the resulting free volume become larger, and the diffusion rate of individual permeating molecules and associated permeating molecules are high, so that the total flux increase. In the liquid boundary layer, the mass transfer coefficient of components increases with feed temperature which causes a decrease of concentration polarization, and then an increase of flux and a decrease of selection factor. In addition, an increase of the vapor pressure of the components of feed with temperature causes both components to desorb rapidly and reduces the activity of both components on the downstream side, resulting in an enhance of flux.

The suitable pervaporation performance of the membrane was obtained at the room temperature (30 °C), especially at low methanol content in feed.

4.4 Effect of feed flow rate

In order to determine if mass transport in the boundary layer is a factor controlling the transport of alcohol from feed to the permeate side of the membrane, the feed flow rate was varied and the membrane performance was evaluated at the different flow rates, maintaining the constant concentration of alcohol in the feed.

The permeate concentration, fluxes and selectivity were determined at three different feed flow rates (3.5, 10, and 17 ml min^{-1}). All experiments in this section were carried out at 30 °C, and downstream pressure of 34 cmHg at six different concentrations of methanol in feed (10 to 60 wt % methanol). The fluxes and selection factors for methanol and water at various feed flow rates are shown in Table C.17 (Appendix C).

Figure 4.4.1 shows the methanol mass fraction in the permeate. At each feed concentration, the permeate concentration increased with a decrease in the feed flow rate.

Figure 4.4.2 shows the effect of feed flow rate on the fluxes. The total flux and methanol flux showed a minor change with a decrease in the feed flow rate. Therefore, the total flux and methanol flux was only slightly affected by feed flow rate change. The water flux was found to increase with an increase in the feed flow rate.

Figure 4.4.3 shows the effect of the feed flow rate on selectivity and PSI. The selection factor increased with a decrease in the feed flow rate as shown in Figure 4.4.3a. The same behavior was obtained in a previous study related to the separation of MTBE aqueous solution using the PP membrane [11]. The high selectivity was obtained at low feed concentration. In this work, the maximum selection factor of 4.08 was obtained at 3.5 ml min^{-1} and feed concentration of 10 wt % methanol. At feed concentration of 10 wt % methanol, slight different PSI was obtained. PSI was found to decrease with an increase in feed flow rate at feed concentration above 20 wt % methanol.

In general, the concentration of methanol, a more permeable component, on the membrane surface is lower than that in the bulk phase. The opposite is true for water which is a less permeable component. A reduction of concentration polarization at high flow rate means that the methanol concentration near the membrane surface was close to the methanol concentration in the bulk. An increase of methanol concentration on the membrane surface with feed flow rate enhances methanol as well as water sorption in the membrane, therefore, membrane swelling increased and the selection factor reduced.

The suitable pervaporation performance of the membrane was obtained at the low feed flow rate (3.5 ml min^{-1}), especially at low methanol content in feed.

4.5 A comparison of previous and present work

In this study, using PTFE/PP membrane for pervaporation of methanol-water mixture, the best conditions give the high performance of the pervaporation system are the concentration of methanol in feed of 10 wt %, downstream pressure of 34 cmHg, feed temperature of 30 °C, and feed flow rate of 3.5 ml min^{-1}. Table 4.1 shows a comparison of present and previous work [37, 38, 39]. PTFE membrane used in this work was found to give the selection factor of 4.08, whereas PDMS-PMHS and HPP membranes used in previous work gave lower values of selection factor, However, PDMS and silicalite-filled PDMS membranes gave better selection factor. The total flux and PSI for PTFE membrane used in this work was found to be significantly higher than those for other membranes. Therefore, the PTFE membrane in this work gives better pervaporation of a methanol-water mixture, in comparison with other membranes reported in previous work.

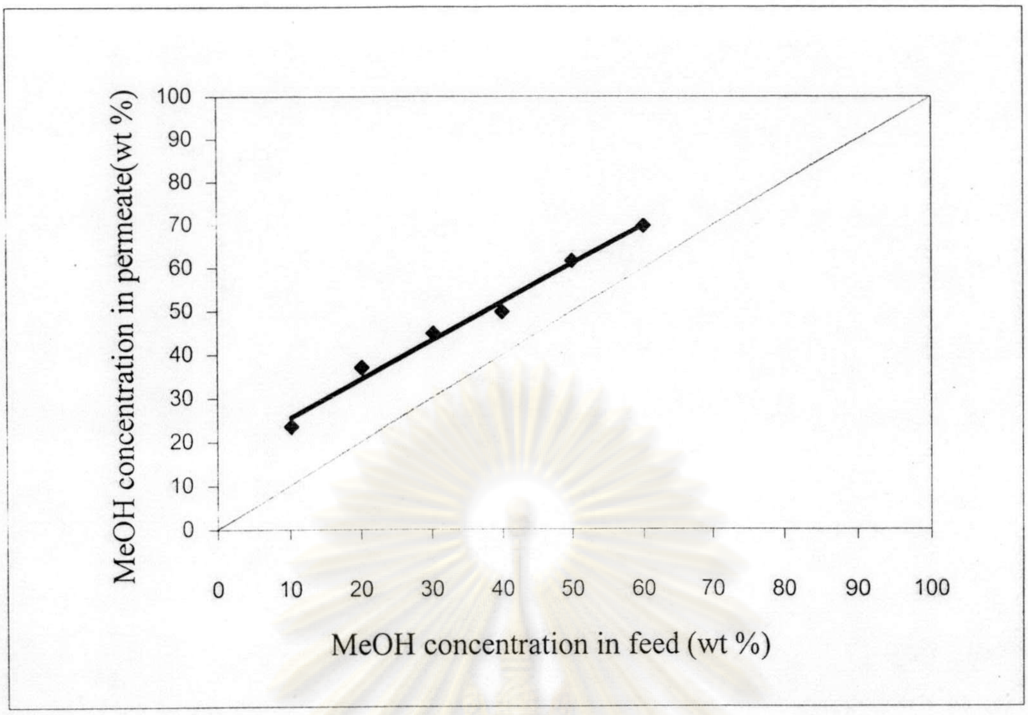

Figure 4.1.1 Effect of feed concentration on permeate concentration in pervaporation of methanol solution at T = 30 °C, F = 17 ml min^{-1} and P = 34 cmHg.

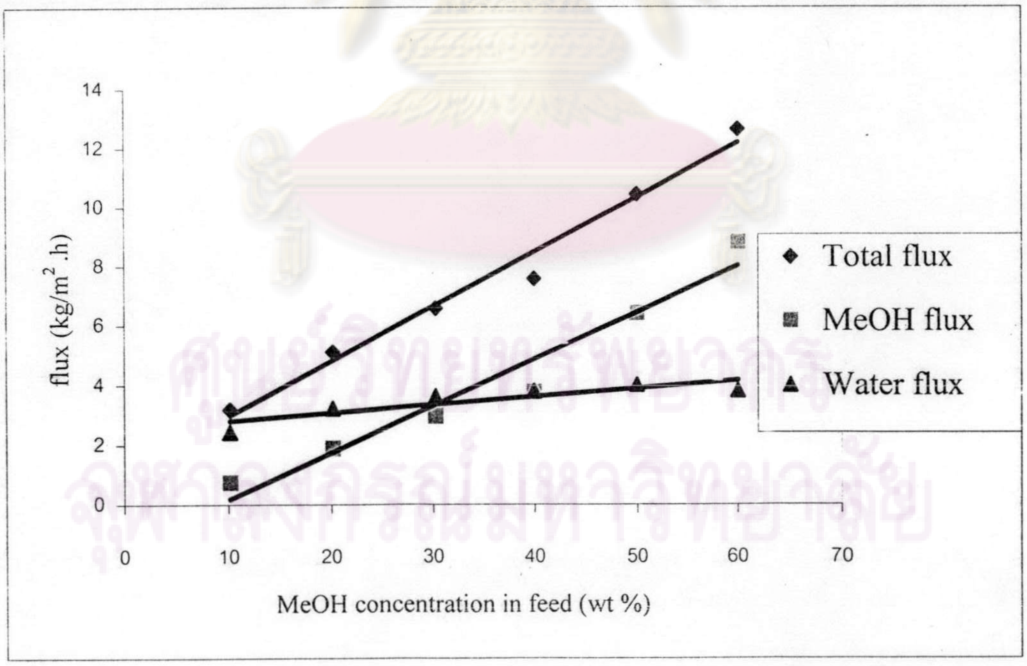

Figure 4.1.2 Effect of feed concentration on fluxes in pervaporation of methanol solution at T = 30 °C, F = 17 ml min^{-1} and P = 34 cmHg.

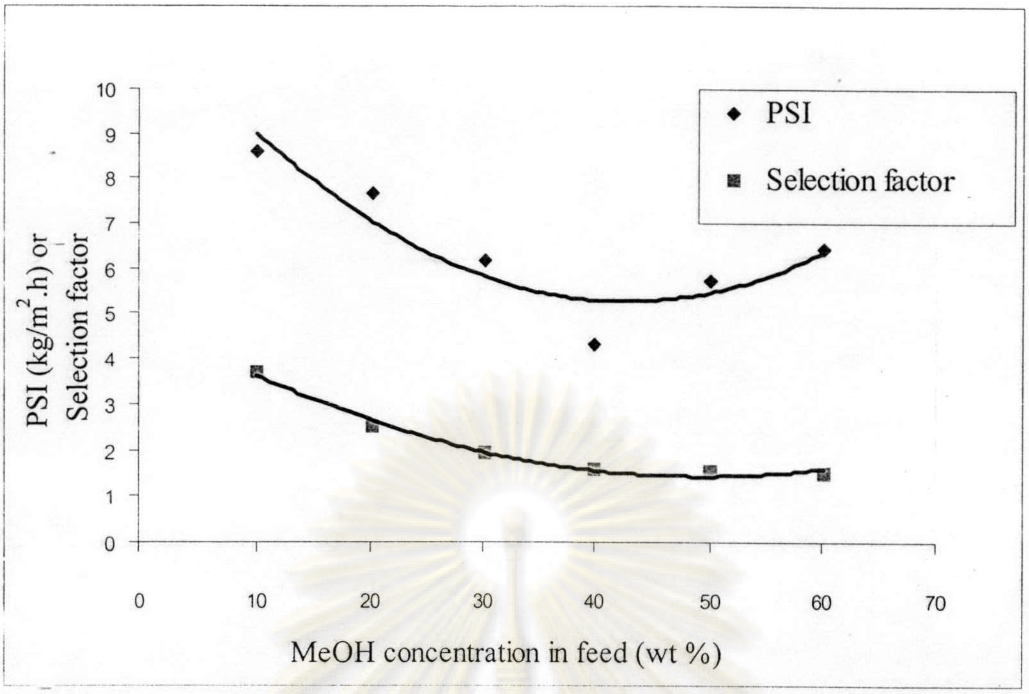

Figure 4.1.3 Effect of feed concentration on selectivity and PSI in pervaporation of methanol solution at T = 30 °C, F = 17 ml min^{-1} and P = 34 cmHg.

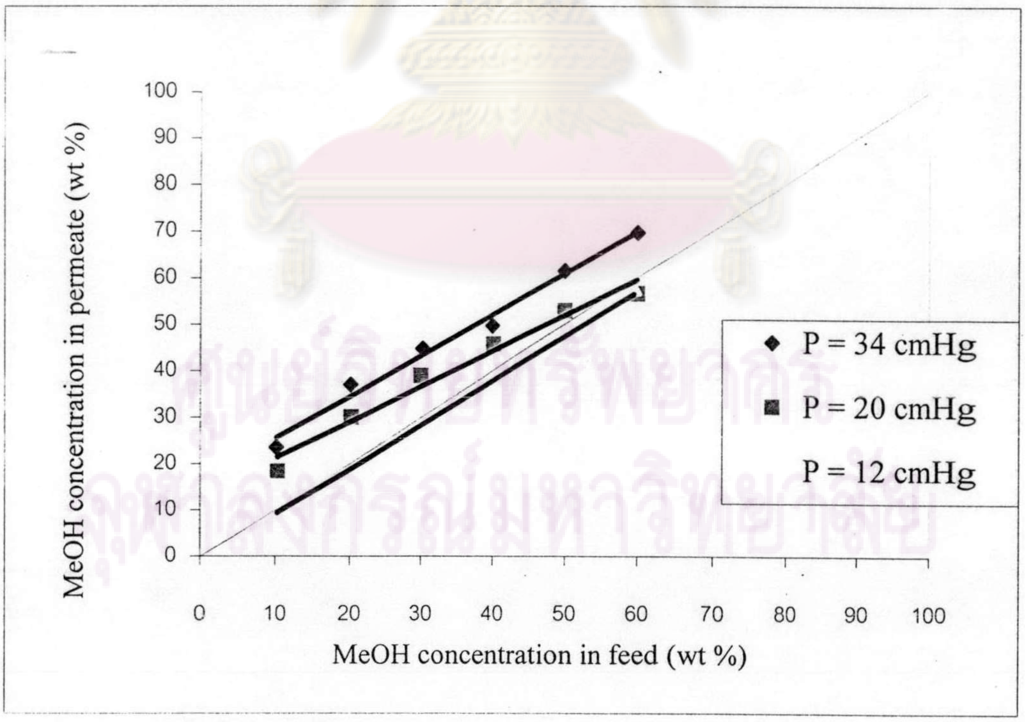

Figure 4.2.1 Effect of downstream pressure on permeate concentration in pervaporation of methanol solution at T = 30 °C and F = 17 ml min^{-1} for six different feed concentrations.

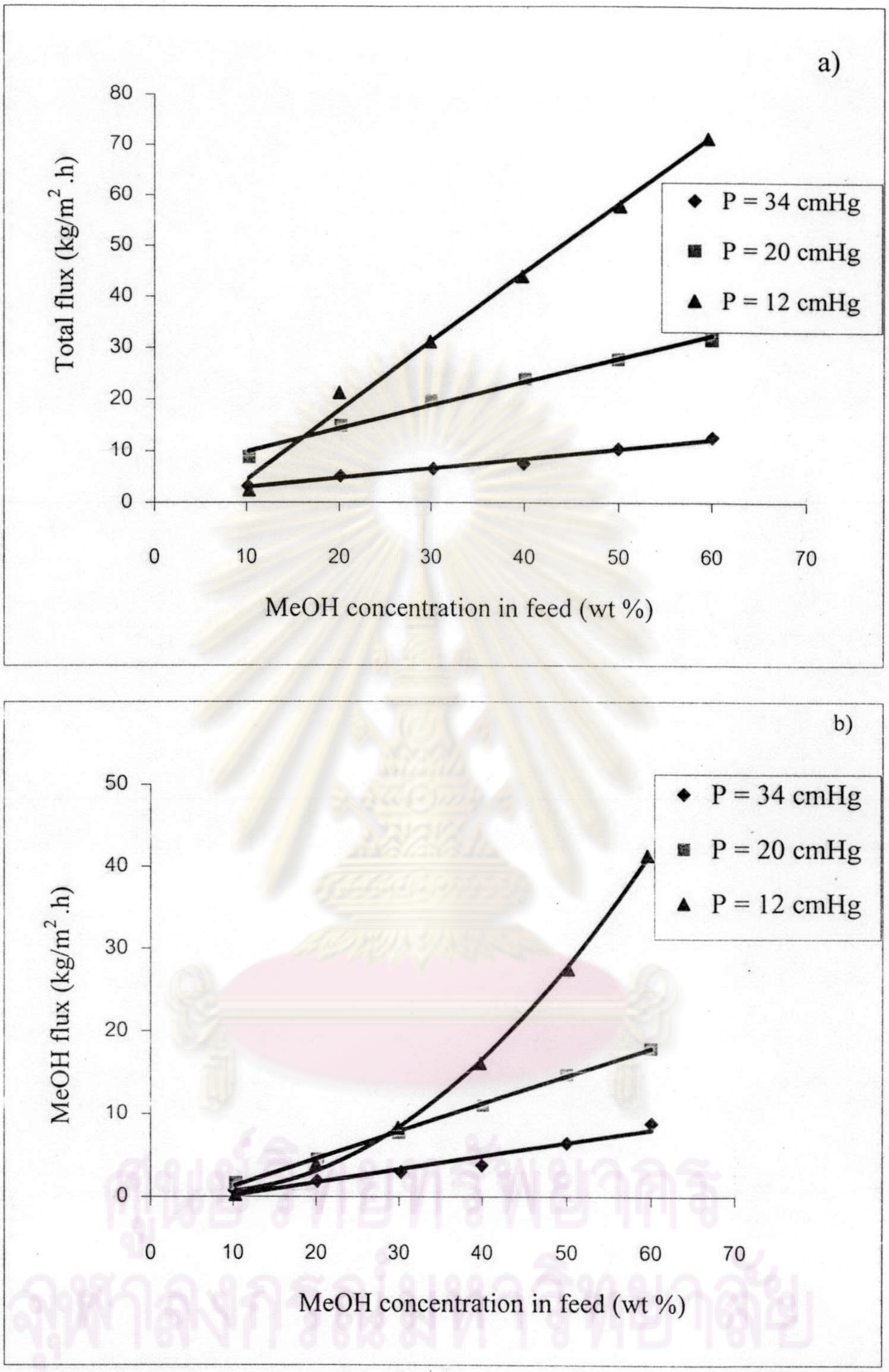

Figure 4.2.2 Effect of downstream pressure on a) total flux, b) MeOH flux and c) water flux in pervaporation of methanol solution at T = 30 °C and F = 17 ml min^{-1} for six different feed concentrations.

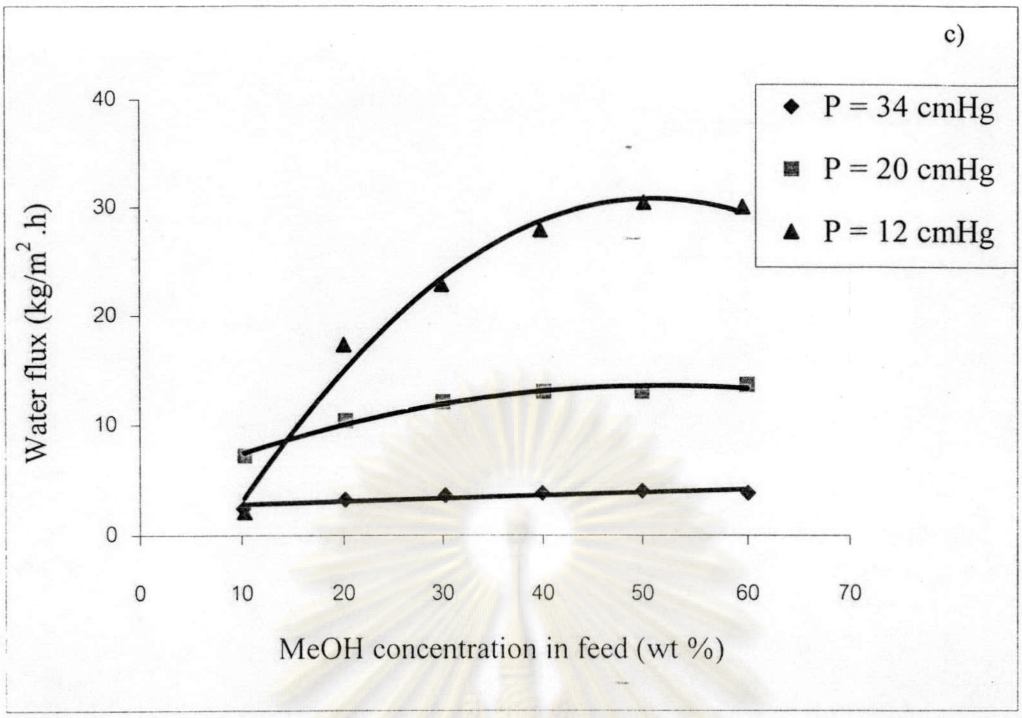

Figure 4.2.2 (continued) Effect of downstream pressure on a) total flux, b) MeOH flux and c) water flux in pervaporation of methanol solution at T = 30 °C and F = 17 ml min^{-1} for six different feed concentrations.

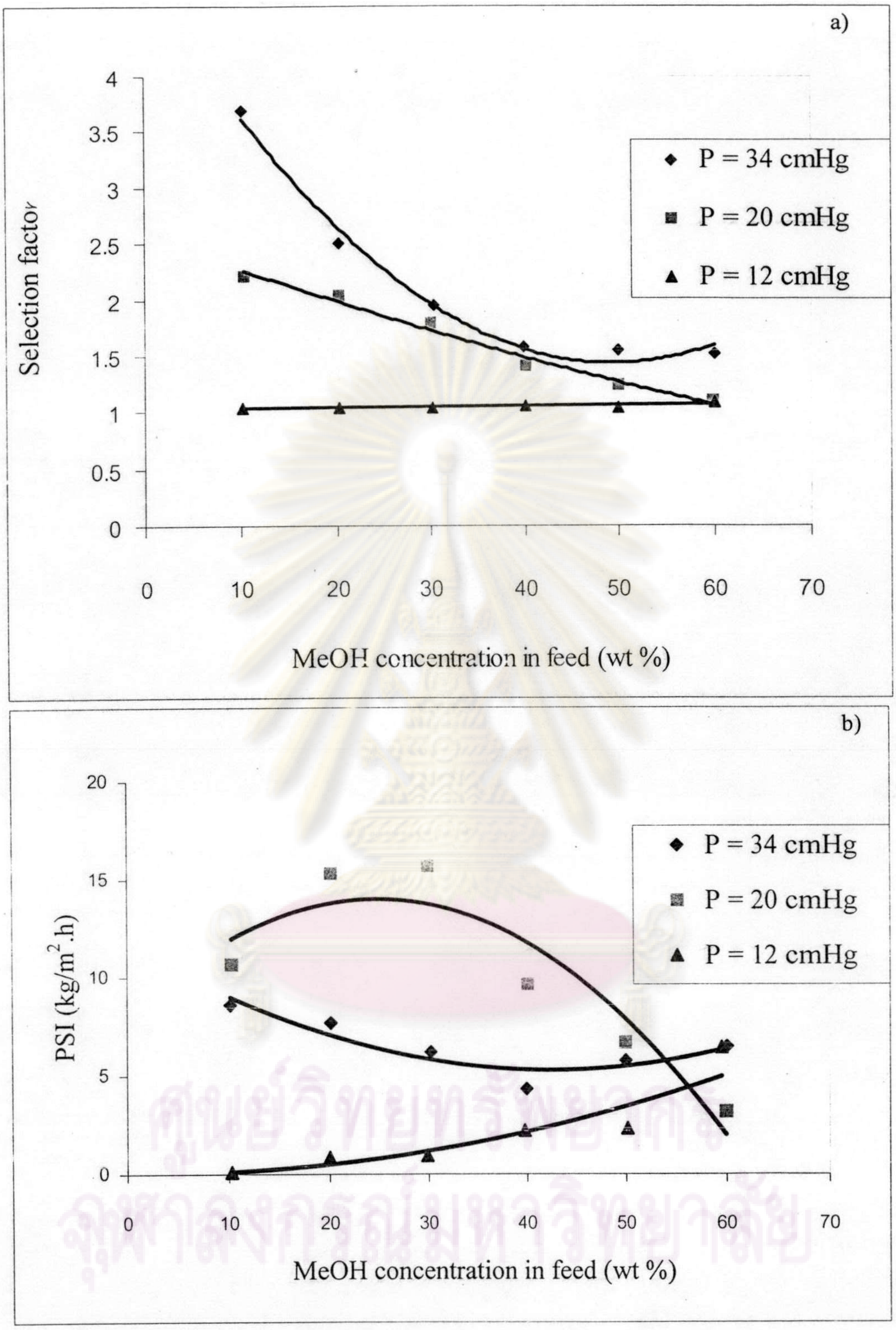

Figure 4.2.3 Effect of downstream pressure on a) selectivity and b) PSI in pervaporation of methanol solution at T = 30 °C, F = 17 ml min^{-1} for six different feed concentrations.

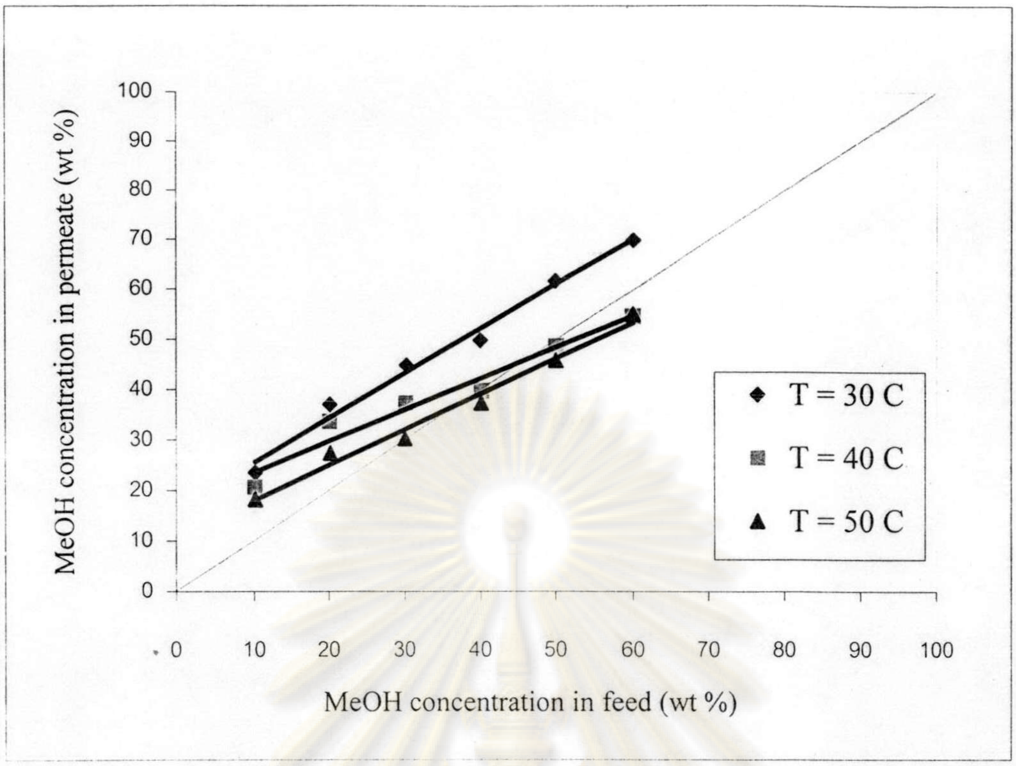

Figure 4.3.1 Effect of feed temperature on permeate concentration in pervaporation of methanol solution at F = 17 ml min^{-1} and P = 34 cmHg for six different feed concentrations.

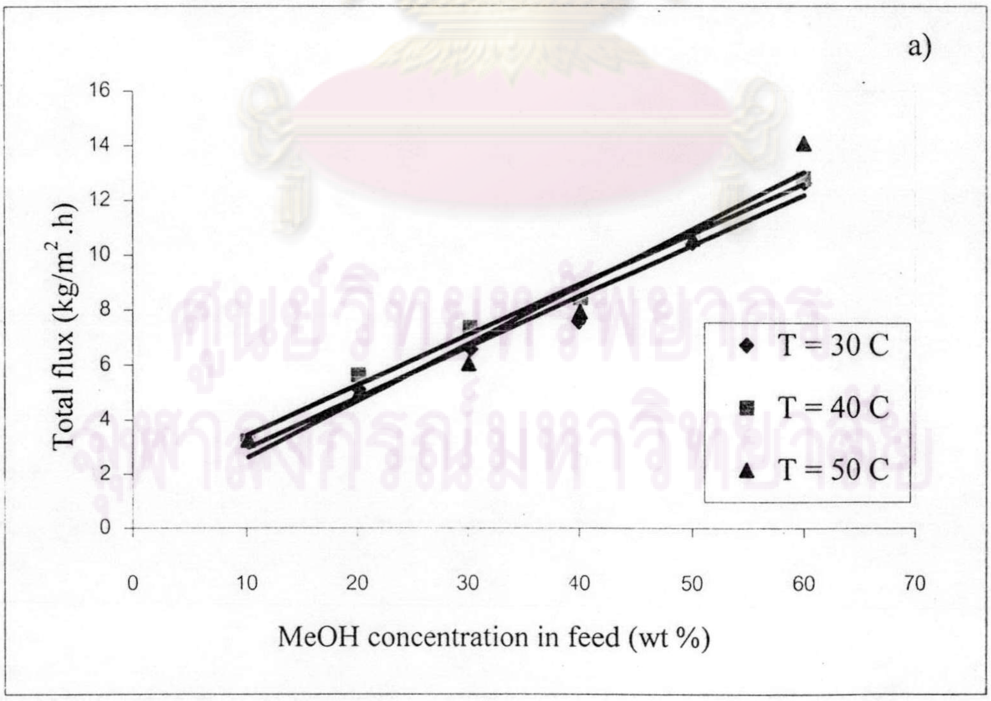

Figure 4.3.2 Effect of feed temperature on a) total flux, b) MeOH flux and c) water flux in pervaporation of methanol solution at F = 17 ml min^{-1} and P = 34 cmHg for six different feed concentrations.

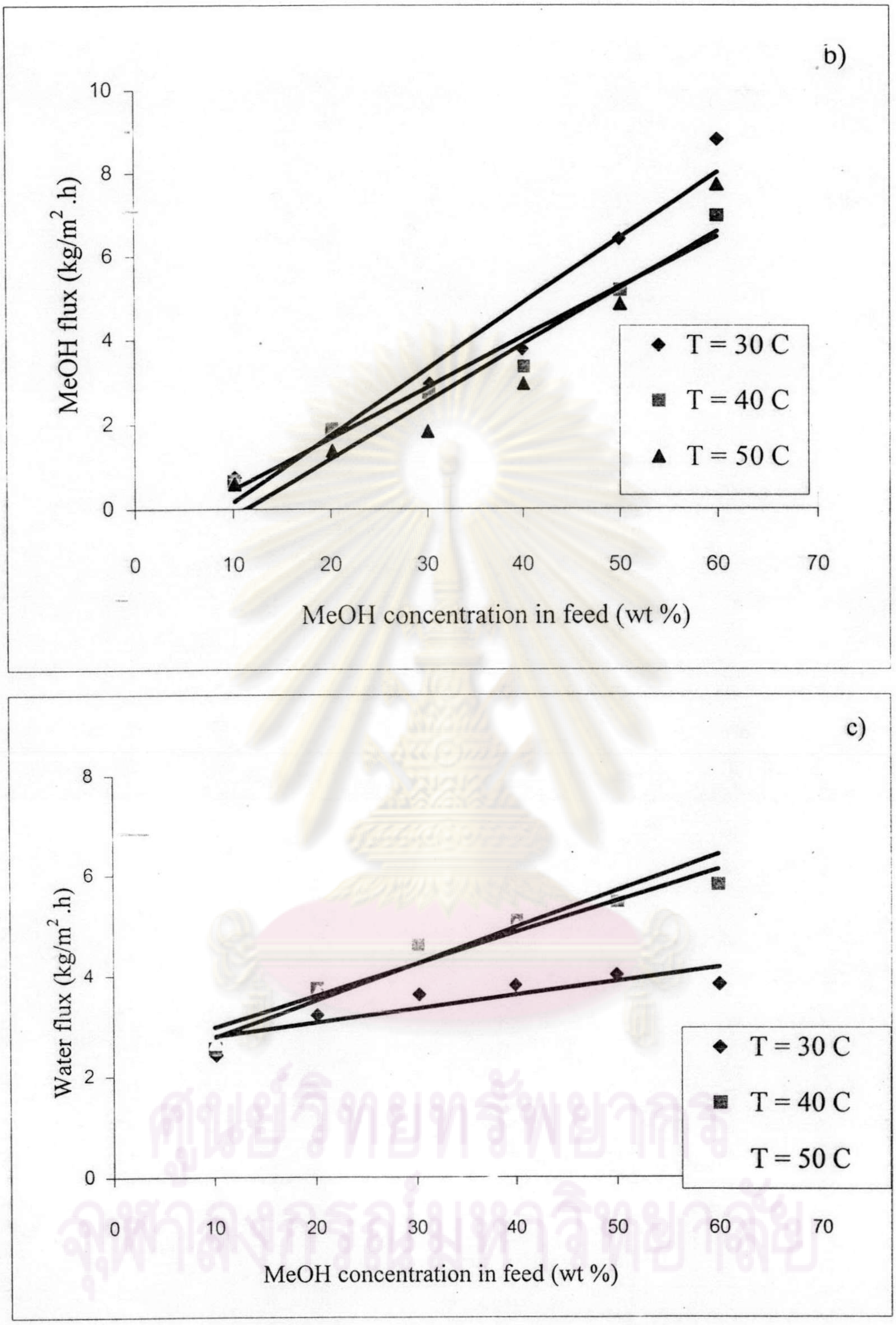

Figure 4.3.2 (continued) Effect of feed temperature on a) total flux, b) MeOH flux and c) water flux in pervaporation of methanol solution at F = 17 ml min^{-1} and P = 34 cmHg for six different feed concentrations.

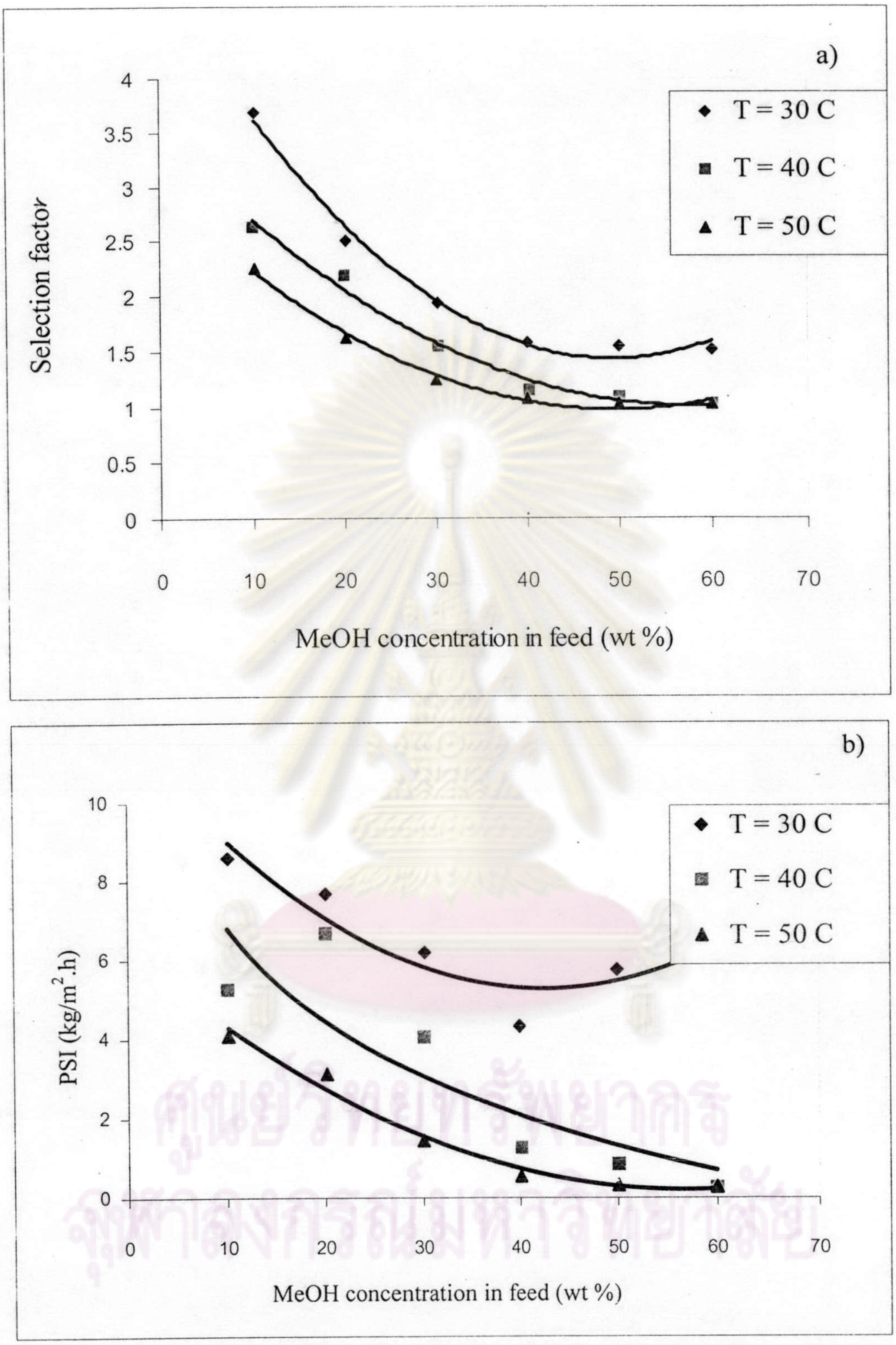

Figure 4.3.3 Effect of feed temperature on a) selectivity and b) PSI in pervaporation of methanol solution at F = 17 ml min^{-1} and P = 34 cmHg for six different feed concentrations.

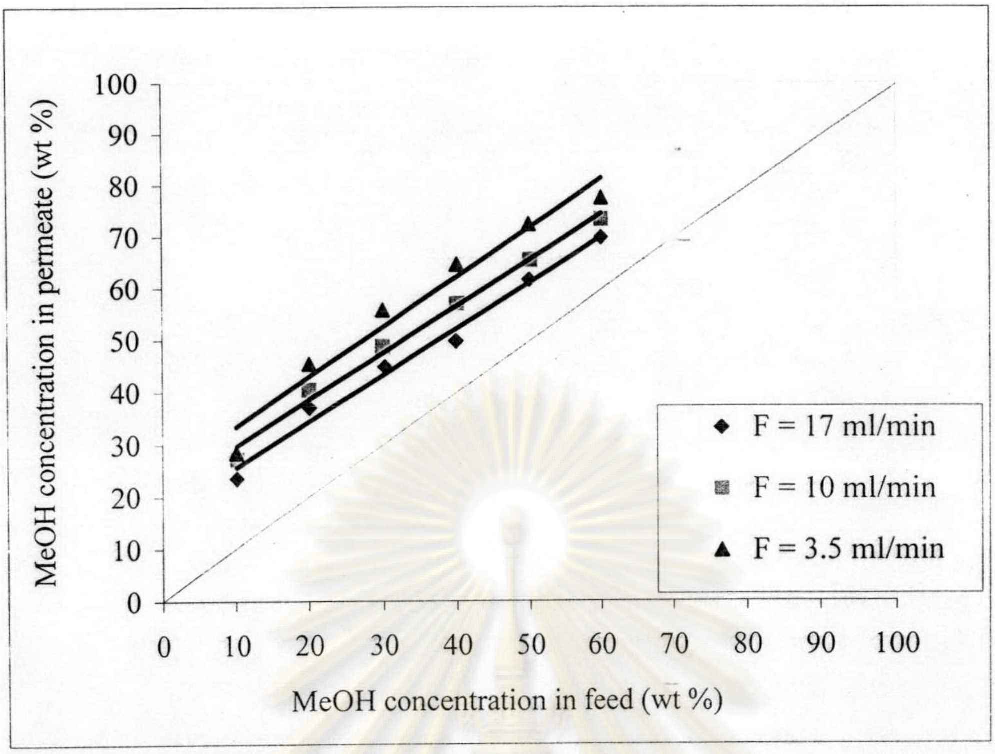

Figure 4.4.1 Effect of feed flow rate on permeate concentration in pervaporation of methanol solution at T = 30 °C and P = 34 cmHg for six different feed concentrations.

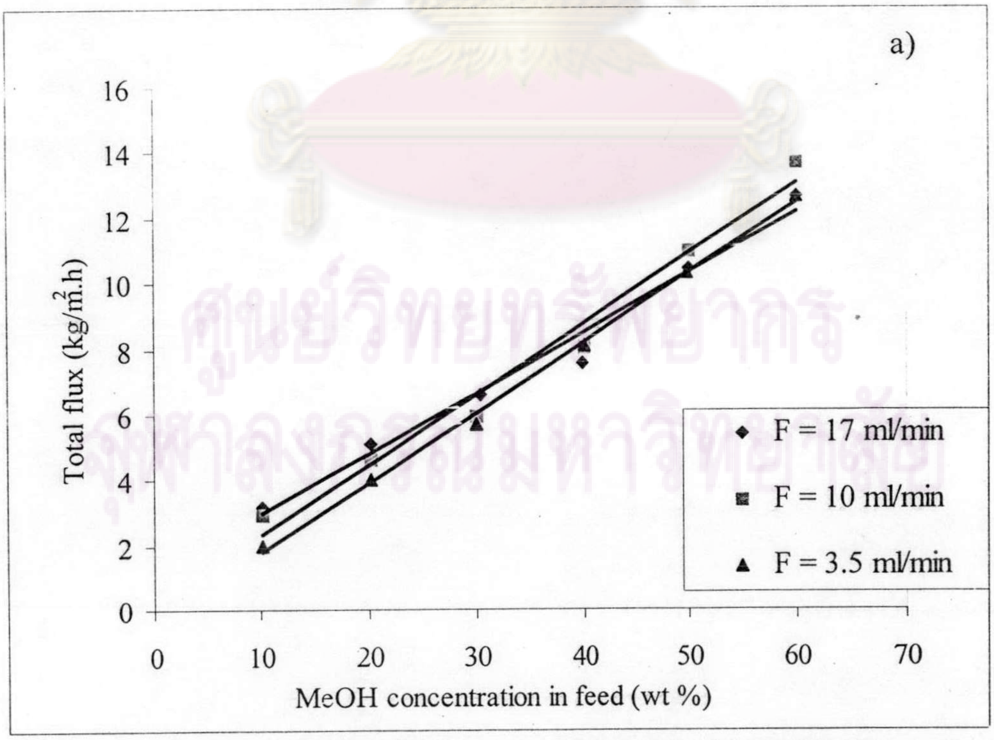

Figure 4.4.2 Effect of feed flow rate on a) total flux, b) MeOH flux and c) water flux in pervaporation of ethanol solution at T = 30 °C and P = 34 cmHg for six different feed concentrations.

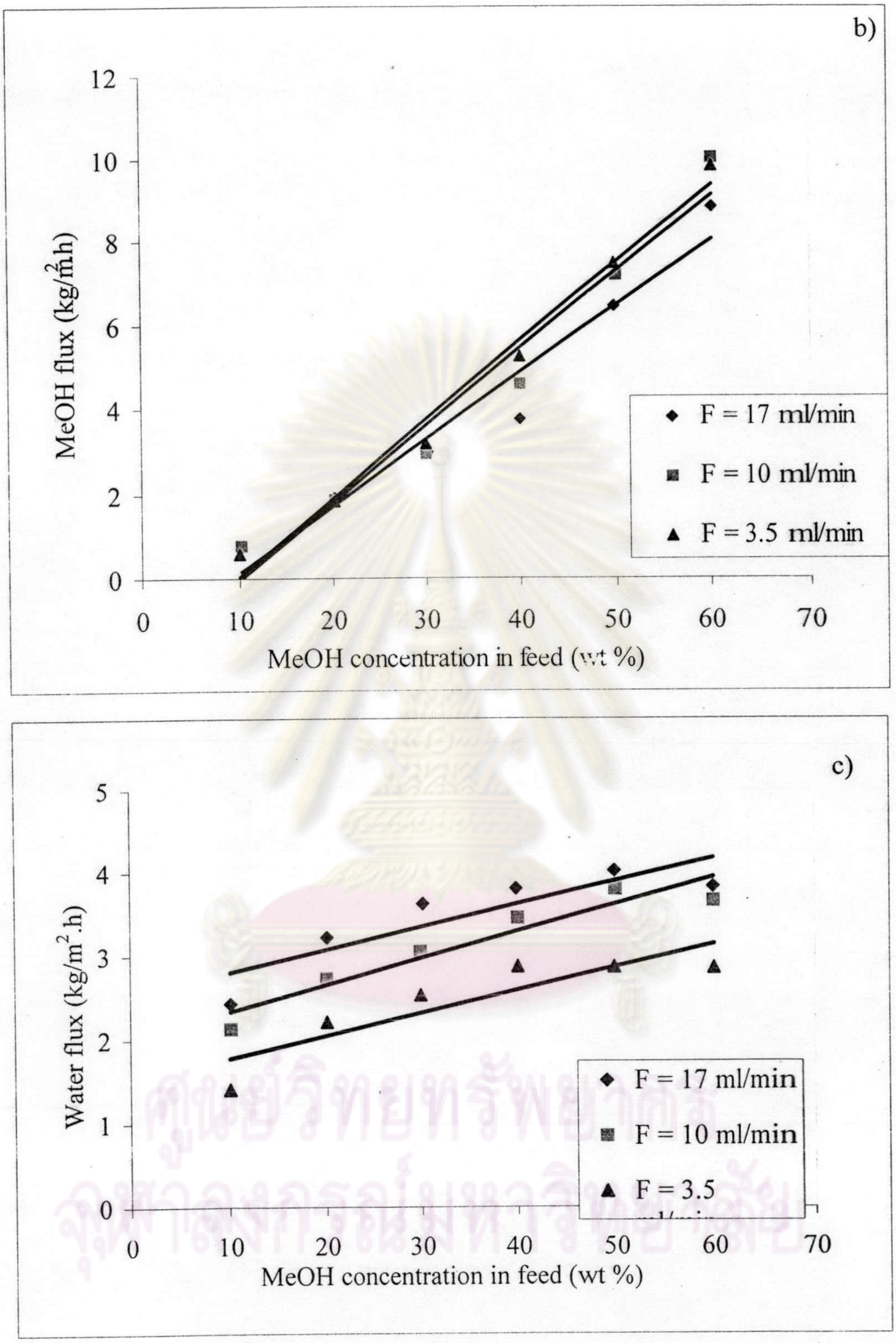

Figure 4.4.2 (continued) Effect of feed flow rate on a) total flux, b) MeOH flux and c) water flux in pervaporation of ethanol solution at T = 30 °C and P = 34 cmHg for six different feed concentrations.

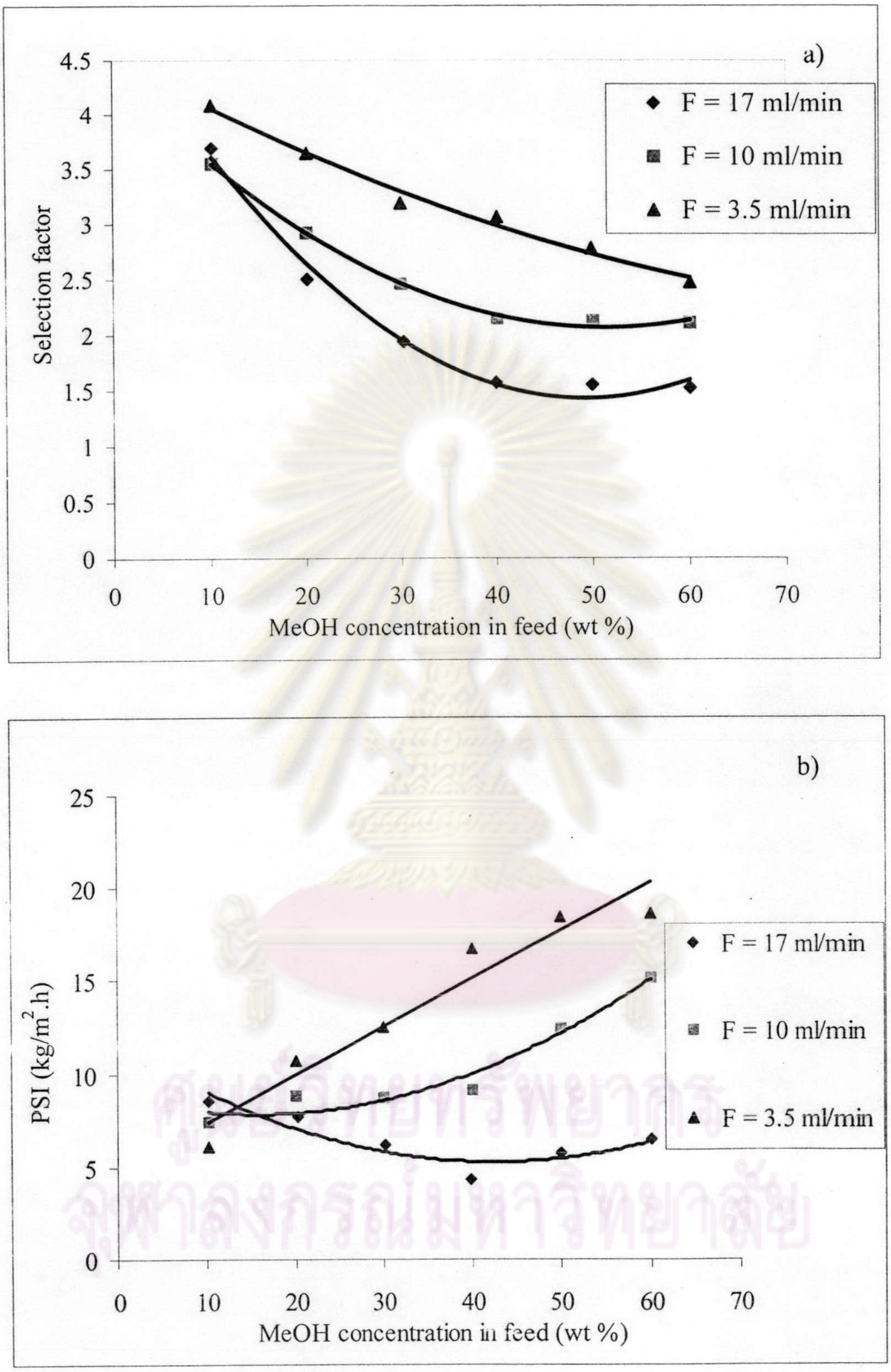

Figure 4.4.3 Effect of feed flow rate on a) selectivity and b) PSI in pervaporation of methanol solution at T = 30 °C and P = 34 cmHg for six different feed concentrations.

Table 4.1 Overview of the pervaporation performance of various hydrophobic membranes in methanol-water system

Membrane	Concentration of methanol in feed (wt %)	Temperature (°C)	Downstream pressure (cmHg)	Flow rate (ml min^{-1})	Total flux (kg m^{-2} h^{-1})	Selection factor	PSI (kg m^{-2} h^{-1})	Reference
PDMS	5.3	22.5	0.08	-	0.02	7.60	0.132	[37]
PDMS/ 30 wt %silicalite	5.3	22.5	0.08	-	0.03	9.50	0.255	[37]
PDMS/ 60 wt %silicalite	5.3	22.5	0.08	-	0.07	13.00	0.840	[37]
PDMS-PMHS	5.0	40.0	0.70	80.0	0.08	2.80	0.144	[38]
HPP	10.0	49.0	9.00	50.0	0.13	3.70	0.351	[39]
PTFE	10.0	30.0	34.00	3.5	1.97	4.08	6.07	[This work]