CHAPTER 4 RESULTS AND DISCUSSION

Following the procedure described in the experimental section, the experiments were conducted to obtain fluxes and permeabilities. The factors affecting permeation of organic compounds through Kapton® polyimide membrane carbonized at 600 °C were investigated. The influence of the dipole moment, size parameter, feed composition, and mode of operation, i.e. pervaporation (PV) and vapor permeation (VP) was considered.

4.1 Single-component permeation

Influence of properties affecting adsorption and diffusion

The fluxes of the organic compounds as a function of the experimental time are presented in Figures 4.1 and 4.2 for PV and VP respectively. For PV, permeation of ethanol and acetone exhibited roughly the same trend; their fluxes steadily increased with increasing time and leveled off within 3 hours. Methanol and isopropanol (IPA) fluxes were relatively stable since the first hour of experiments. The flux for pure methanol (100 wt %) was 1.717 mol/m^2.h, whereas those of ethanol, IPA and acetone were considerably lower, i.e., 0.030 mol/m^2.h (ethanol, 99.5 wt %), 0.009 mol/m^2.h (IPA, 99.8 wt %), and 0.128 mol/m^2.h (acetone, 99.99 wt %). For VP, single–component flux exhibited roughly the same trend with PV, but the fluxes of VP were lower than those obtained from PV. The flux of pure methanol was 1.333 mol/m^2.h, whereas ethanol, IPA and acetone are as follow 0.006 mol/m^2.h, 0.004 mol/m^2 h and 0.186 mol/m^2.h, respectively.

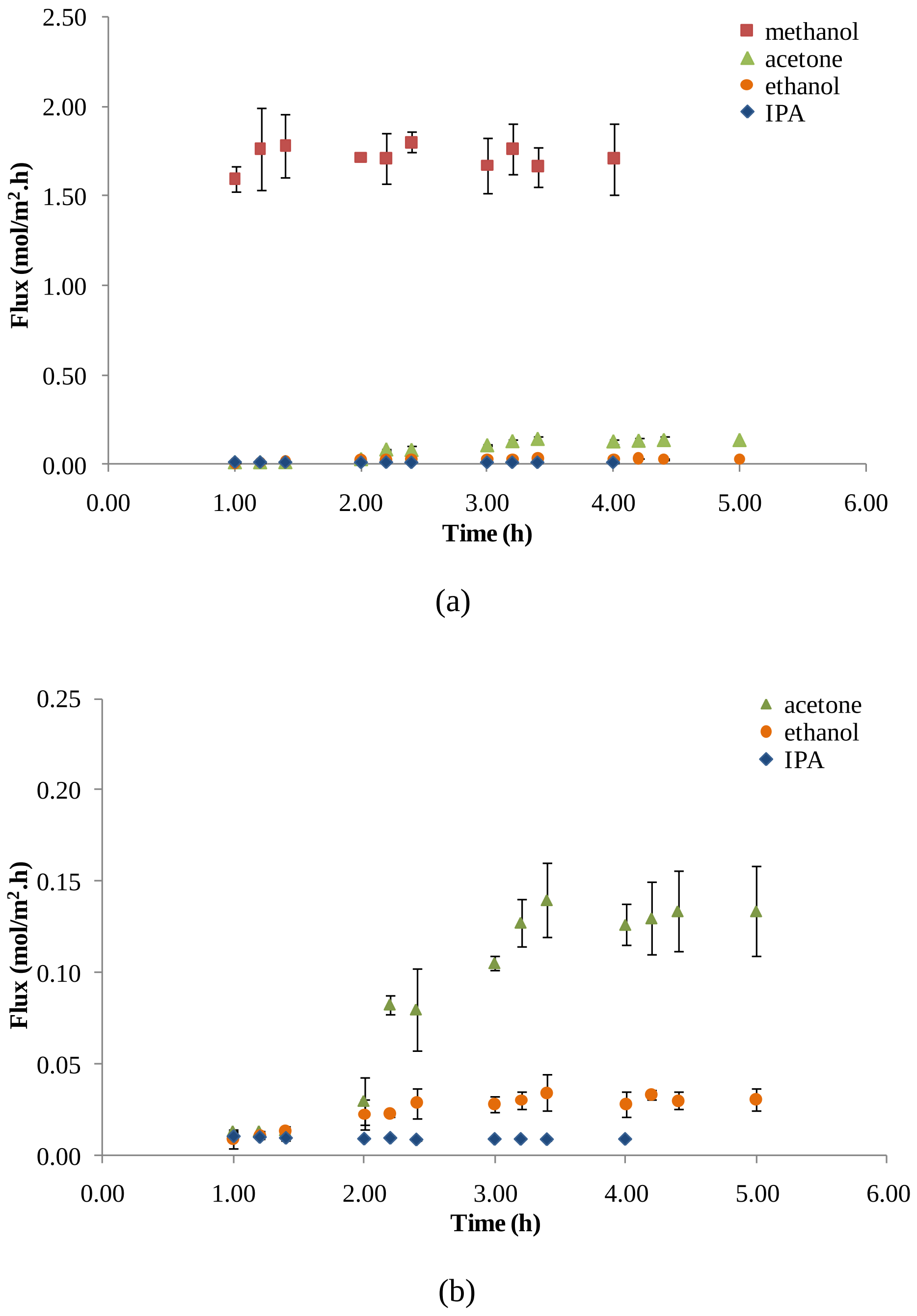


Figure 4.1 Pervaporation fluxes as a function of time for (a) methanol, ethanol, IPA and acetone and (b) ethanol, IPA and acetone.

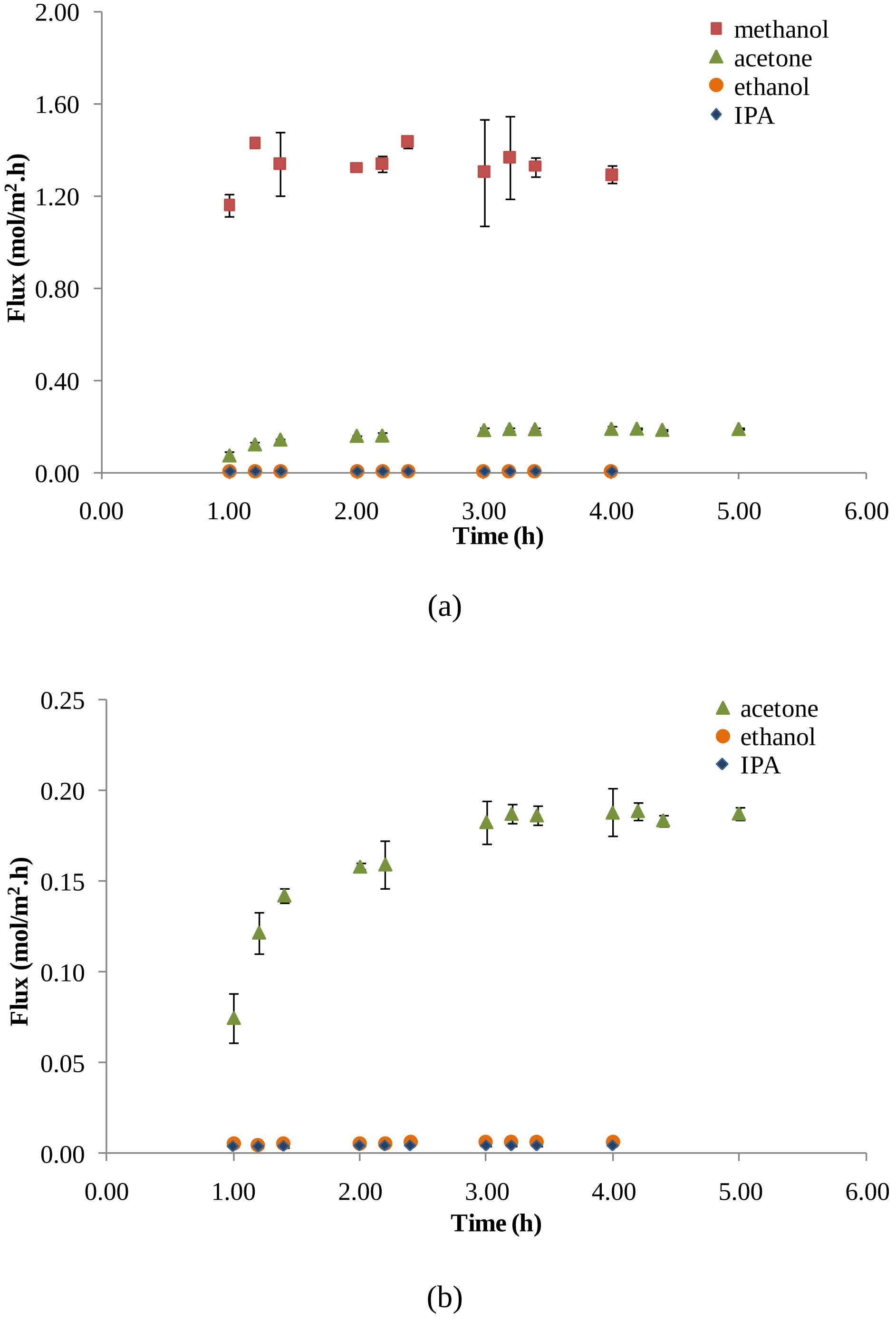


Figure 4.2 Vapor fluxes as a function of time for (a) methanol, ethanol, IPA and acetone and (b) ethanol, IPA and acetone.

The results suggested that both adsorption and diffusion influenced the permeation of a molecule through the carbon membrane. Size parameters presented in Table 4.1, were believed to have an influence on diffusion. The molecular size of a molecule can be characterized in many different ways, by the molecular weight and the kinetic diameter. With the exception of acetone, the permeabilities agreed well with the molecular sizes of the penetrants. Organic compounds with small molecular sizes had higher permeability than that of the larger molecules. Being the smallest molecule, methanol showed the highest flux. Nevertheless, the ability to be adsorbed onto the membrane surface could surpass the diffusion effect which primarily was dependent on size parameters. Adsorption ability was related to the polarity of molecule [13]. Despite its larger kinetic diameter, acetone was more permeable than ethanol. This was likely because acetone was more readily adsorbed onto the hydrophilic surface of the membrane as indicated by its relatively higher dipole moment presented in Table 4.1. In addition, it also had higher permeability than that of IPA, a molecule with approximately the same size, which mainly resulted from the difference in adsorption ability. Based on the dipole moment, acetone was more polarity. The results of permeabilities through membrane were consistent with fluxes as presented in Table 4.2.

Table 4.1 Molecular weight, Molecular diameter, and dipole moment of pure organic compounds. [12, 13 and 18]

Organic Compounds	Molecular weight	Kinetic diameter (nm)	Dipole moment (Debye)
Methanol	32.04	0.380	1.70
Ethanol	46.07	0.430	1.69
Acetone	58.08	0.469	2.98
IPA	60.09	0.470	1.58

Table 4.2 Fluxes and permeabilities of single-component permeation for PV and VP.

Organic Compounds	Permeability × 10^{-9} (mol.m/m^2.h.kPa)		Flux (mol/m^2.h)	
	PV	VP	PV	VP
Methanol	1170	906	1.717	1.333
Ethanol	37.5	6.88	0.030	0.006
Acetone	60.6	88.3	0.128	0.186
IPA	14.1	5.75	0.009	0.004

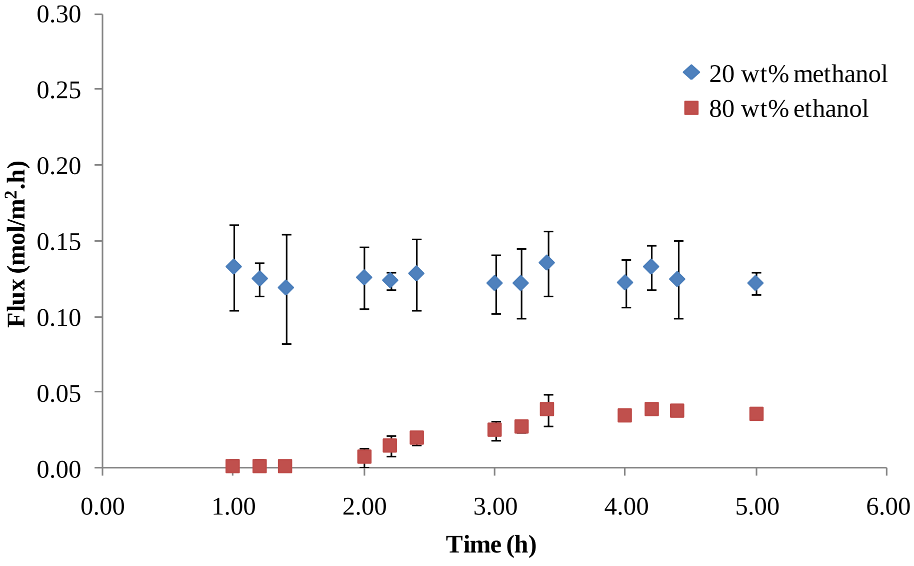
With the exception of acetone, fluxes from PV were higher than fluxes from VP because more steps in permeation through the membrane were required on VP. Their fluxes are present in Table 4.2. Because the feed side of PV contacted with the membrane, the organic compounds could directly evaporate or diffuse into membrane pores. In contrast, organic vapor in VP operation must first be condensed onto the membrane surface before entering the membrane pores. Otherwise, it had to diffuse straight into the membrane pores. However, this explanation was not true for acetone. In this study, driving force did not have effect on difference between PV and VP fluxes because the vapor feed was saturated. For VP, when operating with a saturated vapor phase on the feed side, the driving force was exactly the same as in PV [8].

4.2 Bi-component permeation

As the carbon membrane surface was hydrophilic, it therefore had affinity towards molecule having high dipole moment. In addition, as adsorption was partly influenced by how easy a molecule could condense onto the surface [12], a larger molecule generally was favorably adsorbed. Nevertheless, a smaller molecule was able to permeate through the membrane pores faster than a larger molecule. Both adsorption and diffusion abilities had impacts on the permeation through a carbon membrane as found from the single-component permeation. In this section, the PV and VP experiments using bi-component feeds were carried out to observe the effects from adsorption and diffusion abilities on the competitive permeation.

4.2.1 Influence of molecular diameter

The competitive permeation between two penetrants having comparable adsorption capability was primarily controlled by molecular sieve mechanism. Bi-component permeation was performed using methanol/ethanol (20:80 wt %) as a feed. Kinetic diameter of methanol, 0.38 nm, was smaller than kinetic diameter of ethanol, 0.43 nm, while the difference in their dipole moments was only 0.01 Debye. Though ethanol was larger and likely more adsorbable, methanol fluxes were higher for both PV and VP, in spite of its lower concentration in the feed. Plots of fluxes as a function of time are shown by Figures 4.3 (a) and (b) for PV and VP respectively. For both modes of operations, ethanol fluxes steadily increased with time and leveled off within 3 hours. Methanol fluxes were relatively stable since the first hour of experiments.



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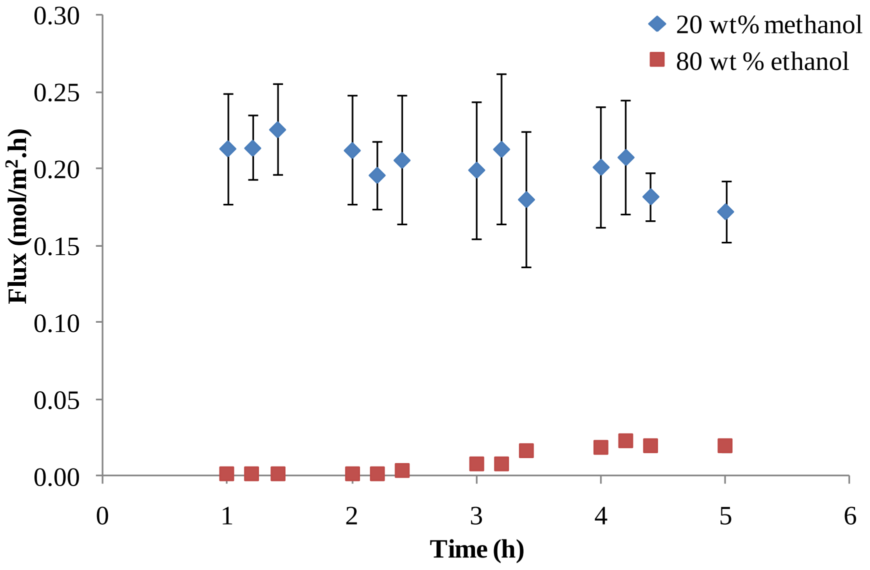

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Figure 4.3 Fluxes as a function of time for methanol/ethanol (20:80 wt. %) mixture (a) Fluxes from PV and (b) Fluxes from VP.

The presence of another organic compound in the feed interfered permeation of each other. This feature was common for microporous membranes [1]. The permeability data presented in Tables 4.2 and 4.3 showed that the presence of ethanol in the feed reduced the permeation of methanol. On the order hand, permeability of ethanol increased. Further analysis revealed that the effect of kinetic diameter was actually suppressed. The ideal permeability ratios, defined as the ratios of methanol permeability to ethanol permeability from single-component feed, were 31.2 and 131.7 for PV and VP, respectively. The ratios obtained from bi-component feed, 5.2 and 13.7 for PV and VP respectively, were smaller. This indicated that a slightly larger kinetic diameter of ethanol, which contributed to a somewhat higher adsorption, lowered the adsorption of methanol. The reduction in methanol adsorption was also compounded by the much higher ethanol concentration in the feed.

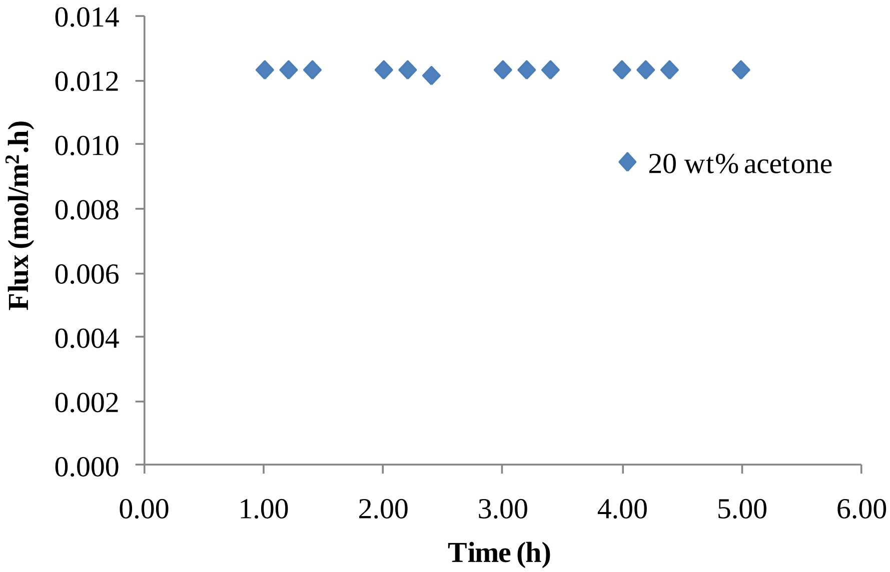
In the presence of methanol, permeability of ethanol was higher when compared with that observed from pure ethanol permeation. This was because methanol increased ethanol diffusion on the surface of membrane pore. A faster diffusing could prevent a slower one from diffusing backwards [15]. In the present work, methanol could follow ethanol and prevented ethanol from diffusing backward to an unoccupied site.

Table 4.3 Fluxes and permeabilities of methanol/ ethanol obtained from bi-component feed

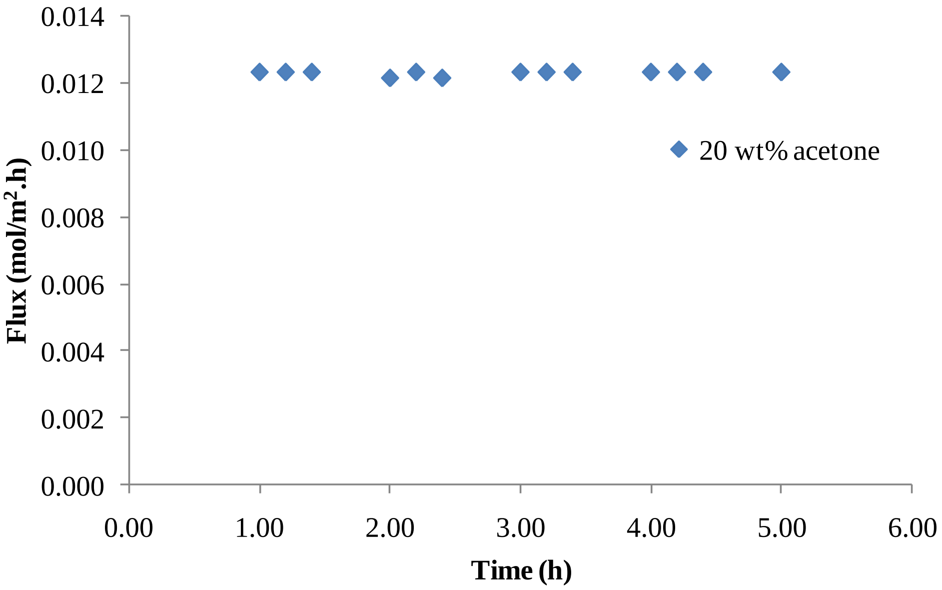
Organic Compounds	Feed composition	Permeability × 10^{-8} (mol.m/m^2.h.kPa)		Flux (mol/m^2.h)	
		PV	VP	PV	VP
Methanol	20 wt %	32.1	49.4	0.126	0.202
Ethanol	80 wt %	6.14	3.60	0.037	0.020

4.2.2 Influence of dipole moment

The effect of adsorption ability was realized from the experiments using two penetrants having similar sizes but different in dipole moments as a feed. The experiment was done by using feed containing acetone/IPA mixture (20:80 wt %). Given approximately the same molecular sizes, substantially higher dipole moment of acetone (2.98 Debye) compared with that of IPA (1.58 Debye) resulted in the blocking of IPA from observable permeating through the membrane. The result showed that the adsorption of IPA was remarkably inhibited by the presence of acetone. The fluxes of acetone/IPA (20:80 wt %) mixture as a function of the experimental time are presented in Figures 4.4 (a) and (b) for PV and VP respectively. For both operating systems, acetone fluxes were relatively stable since the first hour of an experiment.



(a)



(b)

Figure 4.4 Fluxes as a function of time for acetone/IPA (20:80 wt %) mixture (a) Fluxes from PV and (b) Fluxes from VP.

The average fluxes and permeabilities of acetone for PV and VP are reported in Table 4.4. Because the kinetic diameters of acetone and IPA were quite the same, higher adsorption ability of acetone predominated the competitive permeation. The ideal acetone/IPA permeability ratios were 4.3 and 15.4 for PV and VP, respectively. The ratios from bi-component feed experiments could not be obtained because IPA permeation was greatly reduced, resulting in undetectable amount of IPA in permeate. This suggested that the preferential adsorption of acetone and pore blocking had a major impact on the separation mechanism.

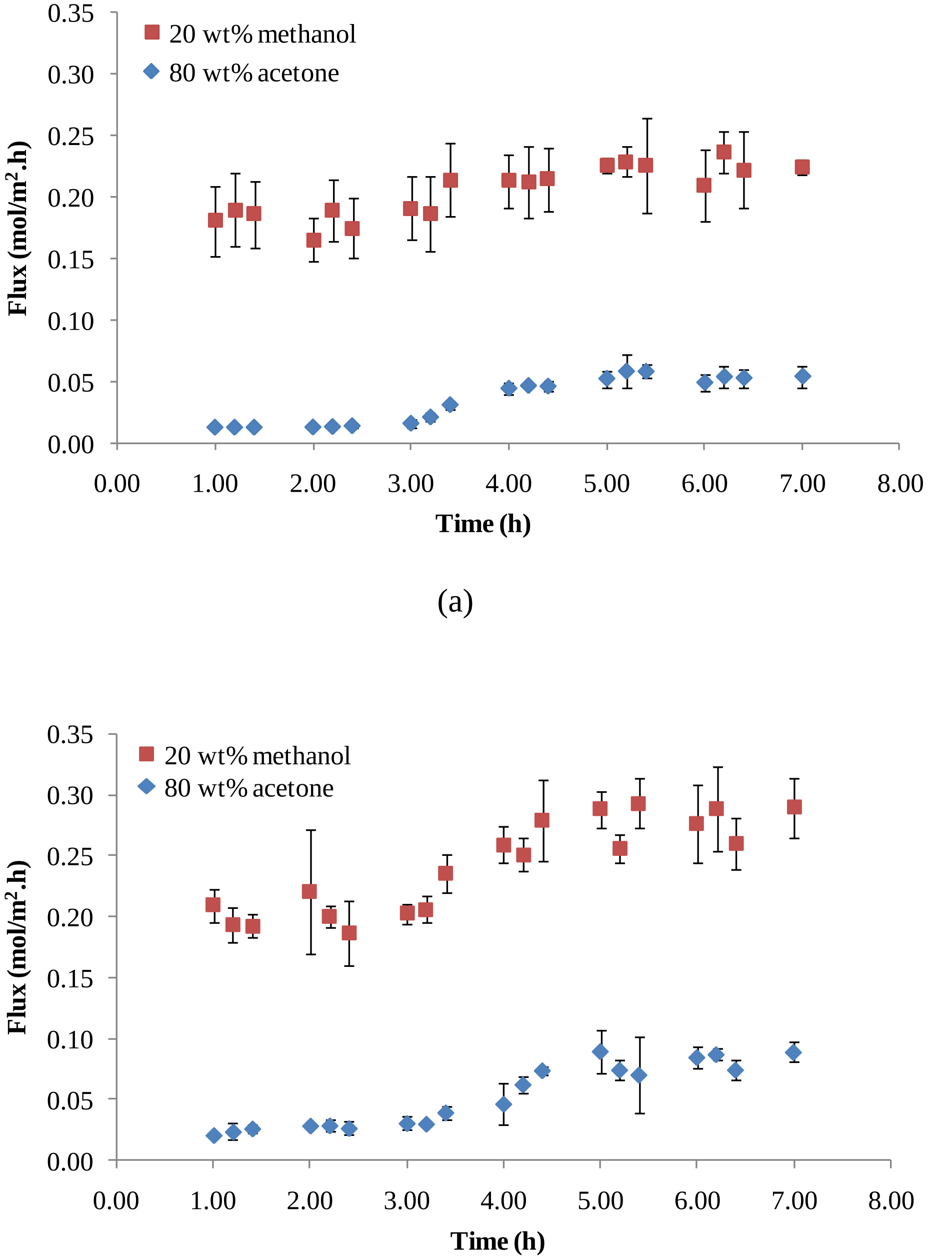
Table 4.4 Fluxes and permeabilities of acetone/IPA obtained from bi-component feed

Organic Compounds	Feed composition	Permeability × 10^{-8} (mol.m/m^2.h.kPa)		Flux (mol/m^2.h)	
		PV	VP	PV	VP
IPA	80 wt %	Undetected by GC	Undetected by GC	Undetected by GC	Undetected by GC
Acetone	20 wt %	1.62	3.31	0.012	0.012

4.2.3 Relative influence between molecular diameter and dipole moment

The relative significance of the adsorption and diffusion abilities could be observed by performing the experiments with two organic compounds having different kinetic diameters and dipole moments.

The molecular sieving could dominate adsorption as discovered from the experiments using feed containing 80 wt % acetone and 20 wt % methanol. This concentration ratio was selected with the intention to observe whether acetone could cover the surface of the membrane and prevent methanol from accessing the membrane surface. The fluxes of methanol and acetone as a function of time are presented in Figures 4.6 (a) and (b) for PV and VP respectively. Although acetone could be more adsorbed onto the membrane surface than methanol because of its higher dipole moment and larger molecular size, it was less permeable than methanol. With the fact that the concentration of acetone was much higher than that of methanol, effect from molecular size was obviously more pronounced than the adsorption.



(a)

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Figure 4.5 Fluxes as a function of time for methanol/acetone (20:80 wt %) mixture (a) Fluxes from PV and (b) Fluxes from VP.

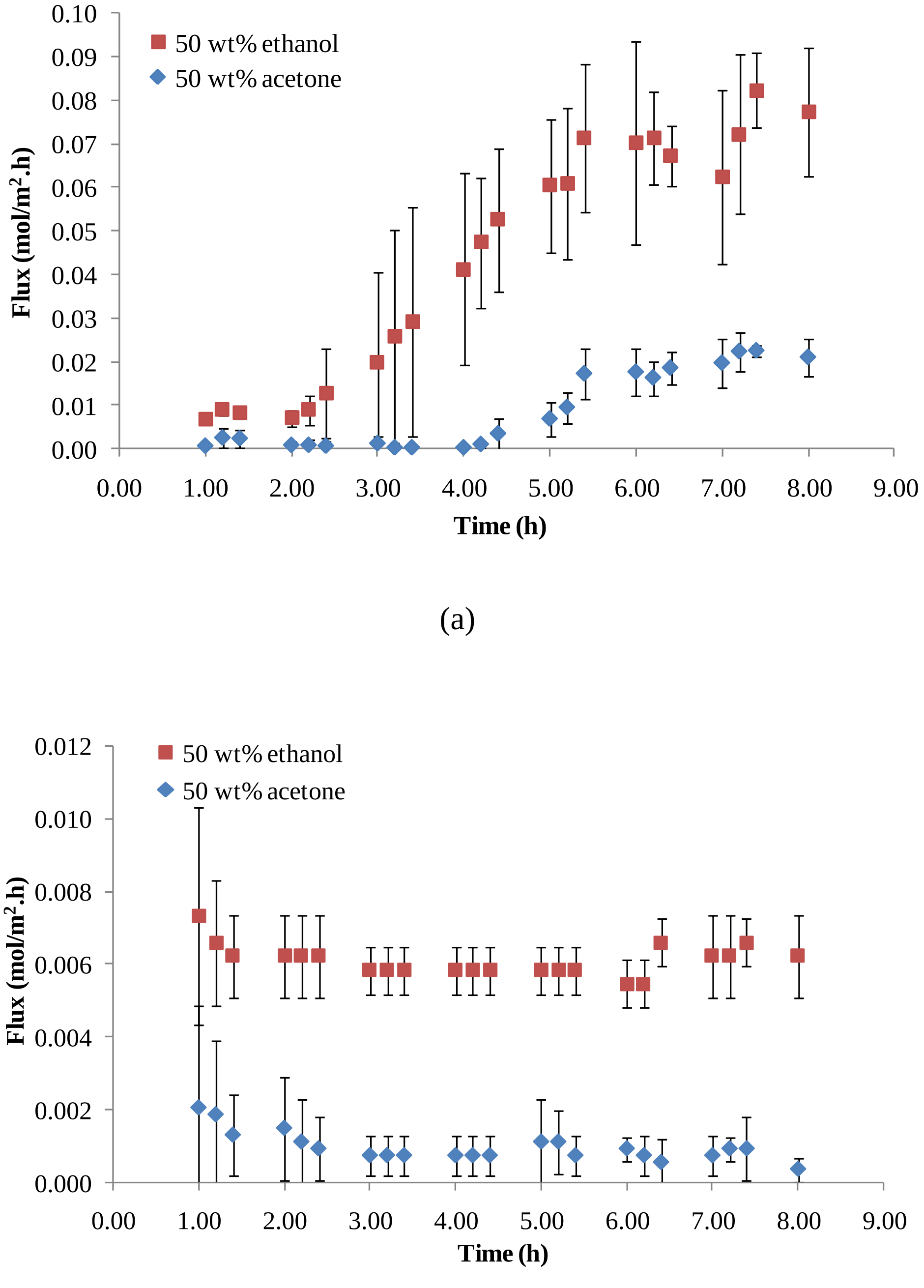
Table 4.5 presents permeabilities of both acetone and methanol from the experiments. Higher permeability of methanol was obtained, contributing to its smaller size. Nonetheless, the presence of acetone in the feed reduced the permeation of methanol as indicated by the reduction in the methanol/acetone permeability ratio. In PV experiments, it decreased from 19.3 for the single-component feed to 10.3 for the bi-component feed. A smaller ratio of 6.4, obtained from the feed containing bi-components, compared with the ideal ratio of 10.3 was also observed in VP experiments. Like the methanol/ethanol permeation, the same conclusion could therefore be drawn, i.e. the higher adsorption ability of acetone suppressed the permeation of methanol.

Table 4.5 Fluxes and permeabilities of acetone/methanol obtained from bi-component feed

Organic Compounds	Feed composition	Permeability × 10^{-8} (mol.m/m^2.h.kPa)		Flux (mol/m^2.h)	
		PV	VP	PV	VP
Acetone	80 wt %	3.50	6.22	0.054	0.081
Methanol	20 wt %	36.2	39.5	0.225	0.279

From single-component experiment, it was found that acetone, despite its larger size, showed higher permeability than ethanol because it could be adsorbed to a larger extent. The experiment with acetone/ethanol (50:50 wt %) mixture as a feed was then performed to observe whether acetone could cover the surface of the membrane and prevent ethanol from accessing the membrane surface. Their fluxes as a function of time are presented in Figures 4.6 (a) and (b) for PV and VP, respectively.

It was quite intriguing that bi-component permeation showed the completely opposite results to those of single-component feed. Despite the fact that acetone was more adsorbable, acetone fluxes were less than ethanol fluxes for both PV and VP experiments as shown by Figure 4.6. When compared with the results observed from single-component experiments, acetone fluxes were drastically suppressed in the presence of ethanol. The opposing permeation rate, observed when both organic solvents were mixed, could possibly be the result of the enhancement in ethanol adsorption by the co-adsorption with acetone. Because of its intrinsically smaller kinetic diameter, ethanol could diffuse faster on the membrane surface and into the pores.



(a)

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Figure 4.6 Fluxes as a function of time for acetone/ethanol (50:50 wt %) mixture (a) Fluxes from PV and (b) Fluxes from VP.

Table 4.6 presents permeabilities of acetone and ethanol which also corresponds to the trend observed using flux values. In PV experiments, the acetone/ethanol permeability ratio reversed from acetone selective, 1.62, for the single-component feed to ethanol selective, 0.12, for the bi-component feed. For VP experiments, the permeability ratio reversed from 12.8 for the single-component feed to 0.09 for the bi-component feed. This was consistent with the fluxes, i.e. the membrane was ethanol selective. In addition, the higher permeability of ethanol in the presence of acetone, when compared with that in the absence of acetone, indicated that the co-adsorption, or the increase in ethanol adsorption could be induced by acetone.

Table 4.6 Fluxes and permeabilities of acetone/ethanol obtained from bi-component feed

Organic Compounds	Feed composition	Permeability × 10^{-10} (mol.m/m^2.h.kPa)		Flux (mol/m^2.h)	
		PV	VP	PV	VP
Acetone	50 wt %	172	9.83	0.020	0.001
Ethanol	50 wt %	1400	11.3	0.072	0.006