CHAPTER 4 :RESULTS AND DISCUSSION

OVERVIEW

Chapter 4 constitutes of 4 main Sections namely Membrane selection (Section 4.1), Single component SO_2/O_2 permeation (Section 4.2), Binary SO_2/O_2 mixture permeation (Section 4.3), and Concluding remarks (Section 4.4). Section 4.1 details the criteria that were used to select the test membranes from diverse suppliers, and the final elimination of poor performing membranes based on experimental screening results. Section 4.2 presents a discussion on the pure component permeation of both SO_2 and O_2. Section 4.3 presents a discussion on the SO_2/O_2 binary mixture permeation. Section 4.4 then gives a conclusion of the chapter.

4.1 MEMBRANE SELECTION

Determination of the ideal membrane material type and the criteria of elimination of poor performing membranes through a screening technique are presented with the thrust of selecting a membrane for the separation of SO_2 and O_2 in the Hybrid Sulphur process.

4.1.1 CHOICE OF MEMBRANE BASED ON MATERIAL TYPE

Gas separation membranes may be classified as is presented in Figure 4.1. The choice of the membrane material type to be employed was based on the proposed feed gas mixture composition given in Section 3.4.2 and the techno-economic feasibility of use of the material in question that is presented in literature.

Appendix H (in hard copy and in CD), presents the VLE properties of the combined streams in need of SO_2/O_2 separation in the Hybrid Sulphur process. The resultant predicted combined vapor phase stream composition range based on the optimum flash temperature range of (27.6°C - 57.38°C) was (9.35 mol % – 18.16 mol %) SO_2 and (90.54 mol % - 81.23 mol %) O_2. It would be economically reasonable to employ a membrane that would preferentially allow permeation of the minor component (SO_2) in the feed stream, the justification being that much less membrane areas would be required to permeate the minute component (SO_2) in contrast to the area requirements that would be needed to permeate the major bulk constituent (O_2) (Javaid, 2005:221). Thus the ideal membrane type for the separation of SO_2/O_2 in the present context would be one that preferentially favors the transport of SO_2. It is perceived that ultra thin sheets made into a tubular membrane configuration would be suitable for the industrial application, though a flat sheet membrane was used in the laboratory scale experiments. SO_2 would permeate radially through the tubular unit and allow recovery of an SO_2 rich stream on the outer of the tube whilst the O_2 rich stream would be recovered at the inner end of the tubular membrane. However a disadvantage that surfaces is the need to recompress the permeated SO_2 from atmospheric pressure to almost 3 bar partial pressure prior to introduction to the anolyte tank in the industrial sceanario.

Figure 4.1 presents the available membrane types that could achieve the SO_2/O_2 separation. Table 4.1 then presents the separation mechanisms employed by the respective membranes and a justification for the membrane material type selection.

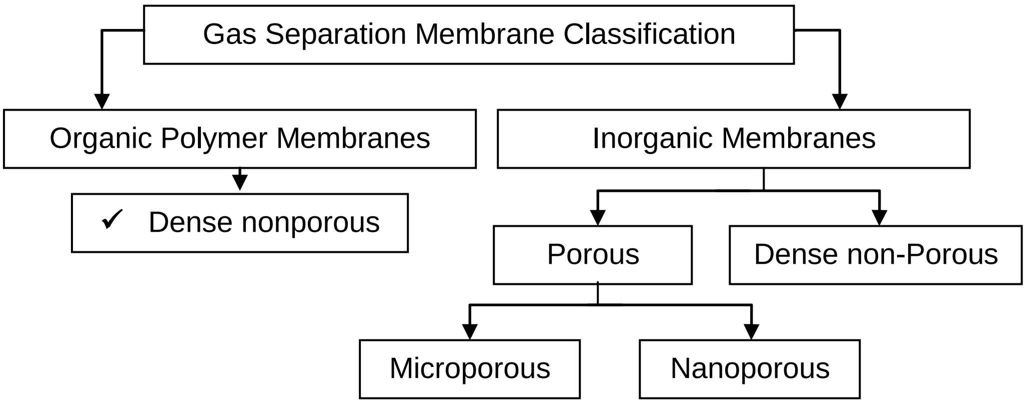


Figure 4.1 Membrane classification

Table 4.1 Characteristics of different membrane types

Organic Polymer	Inorganic		
Dense non-porous	Porous Micro-porous	Porous Nano-porous	Dense non-porous
a) Employ a solution diffusion mechanism(1) b) Solubility selectivity (Selectivity based on material-component interaction rather than molecular size) dominates in rubbery polymers(2) c) Glassy polymers generally exhibit diffusivity selectivity (molecular seiving mechanism), though exceptions exist with glassy polymers with large free volumes where solubility selectivity dominates(1)(2)	a) Carbon molecular sieves and zeolites employ a size exclusion mechanism for separation(3)	a) Selective Surface Flow membranes that selectively permeate the larger and more polar components(4) b) Employ a selective adsorption - surface diffusion – desorption mechanism(4)	a) Dense ceramic membranes which allow component transport in ionic form at temperatures ranging from 600°C-1000°C(3) b) Dense ceramic protonic membranes which are H_2 specific and allow component transport in ionic form at temperatures ranging from 500°C-800°C(3) c) Dense metallic membranes which separate components within a temperature range of 300°C-600°C(3)

(1) Javaid, (2005:221); (2) Stern & Fried, (2007:1037); (3) van der Donk, (2008 :7) ; (4) Sircar *et al*. 1999 :2081)

With reference to Table 4.1 all four different membrane types to some extent have the potential of separating SO_2 from O_2, however there was need to select a membrane type that:

1) Preferentially permeates SO_2 and leaves behind O_2.
2) May be used on large scale commercial applications.
3) May easily be assembled into modular form so as to reduce foot print requirements.
4) May achieve separation at the desired operating conditions (15°C-55°C, laboratory scale and 27.6°C – 57.38°C proposed industrial scale)

The dense non-porous inorganic membranes were disqualified by the temperature range (300°C-1000°C) within which separation occurs. It was intended to operate at temperatures below 60°C in the present study. The micro-porous inorganic membranes would preferentially allow permeation of the smaller O_2 molecule (kinetic diameter = 3.46Å (Breck, 1974:636)) rather than the desired SO_2 molecule (kinetic diameter = 3.6Å (Breck, (1974:636)) because of the size exclusion mechanism employed. Yet nano-porous inorganic membranes would preferentially permeate SO_2 which is larger (kinetic diameter = 3.6Å) and more polar (Dipole moment = 1.6 debye (Bae & Lee, (2005:102)) compared to O_2 (kinetic diameter = 3.46Å, dipole moment = 0 debye (Bae & Lee, (2005:102)), the manufacturing cost and the membrane's durability have confined its application to small scale specialty applications (Koros, 2004; Scholes *et al*. 2012:16). Dense non-porous organic polymer membranes may allow either SO_2 or O_2 to preferentially permeate through solubility or diffusivity selectivity respectively. The expected differing (SO_2-polymer) and (O_2-polymer) interactions evidenced by the gases' differing lennard jones constants and critical temperatures indicate the possibility of separating SO_2 and O_2 through the solubility selectivity transport mechanism employed by the rubbery dense non—porous polymer membranes and some glassy dense non-porous polymers (Stiel & Thodos, 1962:236; Bae & Lee, 2005:102; Stern & Fried, 2007:1037). Solubility selectivity would favor the transport of the more interactive SO_2 molecule. The task at hand is to select a polymer type that would favor SO_2 permeation based on expected gas-polymer interactions derived from both the polymer and gas properties. Most commercial applications have employed dense non-porous polymers for gas separation because of their ease of manufacture into modules which translates to reduced foot prints (Scholes *et al*. 2012:16). Dense polymeric membranes were thus deemed perfect candidates for the separation in question.

4.1.2 CHOICE OF MEMBRANES BASED ON INTRINSIC PROPERTIES

Selection of the ideal membrane to undertake a particular gas separation is a function of both the membrane material and the nature of components to be separated. Solvay, a major polymer manufacturer highlights that present day gas separation membranes are synthesized from both Sulfone polymers and Fluoropolymers (Solvay, 2012a). Membranes chosen for the present study were all either Sulfone or Fluoro based. Table 4.2 presents different membrane intrinsic properties that were used to justify the selection of the membranes used in the present study. The commercial availability of the membrane was also considered.

Table 4.2 Intrinsic properties of selected membranes

Membrane	Permeability(Barrer)				Resistance to H_2SO_4	Free Volume(%)	Polymer	Commercial availability(Supplier)
	N_2	SO_2	O_2	CO_2				
Hyflon F			4.6(7)		Excellent(7)	-	Fluoro(16)	Solvay(7)
Halar	0.03(4), 0.058(5)		0.137(4), 0.145(5)	1.91(5)	Excellent(8)	1.20**	Fluoro(8)	Solvay(8)
Nafion 117	*		*		Excellent(9)	3.30 - 3.7(11)	Sulfone(9)	Dupont(10)
Hyflon M	1.52(6)	3.04(6)	4.6(6)	13.71(6)	Excellent(6)	-0.08**	Fluoro(15)	Solvay(6)
Udel Polysulfone	0.24(1)		1.38(1)	5.7(1)	Excellent(1)	15.20(12)	Sulfone(1)	Solvay(1)
Teflon AF 2400	490(2), 480(3)		990(2), 990(3)	2800(2)	Unknown	37.00(13)	Fluoro(14)	Dupont(2)

(1) (Solvay, 2011:39); (2) (Biogeneral, 2012); (3) (Park & Lee, 2008:652); (4) (Massey, 2003:76); (5) (Western Analytical, 2012); (6) (Solvay, 2012b:12); (7) (Solvay 2008:22); (8) (Solvay, 2006:22); (9) (Orme & Stewart, 2009:512); (10) (Dupont, 2009); (11) (Sodaye *et al*. 1997:985); (12) (Drodten & Schedlitzki, 2011:131); (13) (Nunes & Peinemann, 2006:60); (14) (Koev, 2011); (15) (Solvay, 2012b:4); (16) (Solvay 2008:3) *Humidity dependent permeability graph in Appendix E; ** Calculation in Appendix C

Table 4.3 Properties of gases

Properties	Gases			
	N_2	SO_2	O_2	CO_2
Kinetic Diameter (Å)	3.64(1)	3.60(1)	3.46(1)	3.30(1)
Lennard Jones Constant ε/k (K)	97.20(2)	347(3)	122.00(2)	191.00(2)
Critical Temperature T_c (K	126.20(4)	430.75(4)	154.58(4)	304.21(4)

(1) (Breck, 1974:636); (2) (Stiel & Thodos, (1962:236); (3) (Meyer & Thodos, 1962:532); (4) (Poling *et al*. 2008 :2-138)

The aim was to employ a membrane that offers the lowest possible O_2 permeability, whilst simultaneously offering the highest possible SO_2 permeability. Table 4.2 only provides the O_2 permeability in all membranes with the exception of Nafion 117 which has a humidity dependant O_2 permeability presented by Catalano *et al*. (2012:6313) and given in Appendix E. SO_2 permeability is only given for Hyflon M (Perfluoroalkoxy) which acts as a standard membrane upon which both the experimental permeabilities of O_2 and SO_2 can be compared. It may be perceived that Hyflon F would exhibit similar gas separation properties as Hyflon M, since Hyflon F (MFA) is regarded to belong to the perfluoroakoxy class, the difference being melting point (Massey, 2003:91).

Javaid, (2005:221) suggested that since diffusivity selectivity favors the permeability of the smaller molecules, to accomplish separation based on preferential transport of the heavier molecule, the polymer in question must possess a large enough free volume such that the diffusivity ratios of the two components is pushed to unity (Javaid, 2005:221). In such a scenario, solubility selectivity then dominates and thus the heavier molecule permeates preferentially.

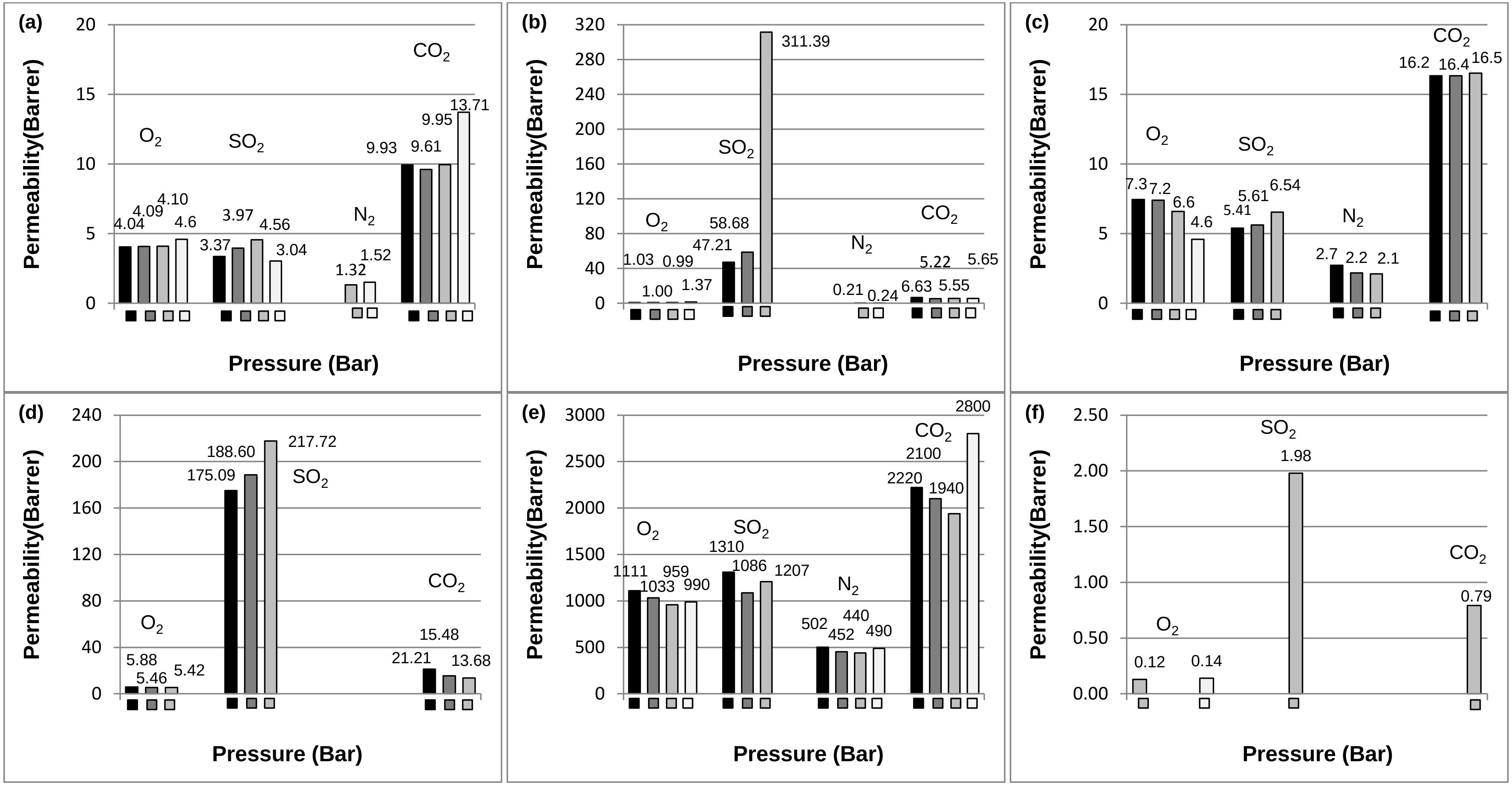
Scrutinizing Tables 4.2 and 4.3, the permeability of all gases in Hyflon M tends to increase with decreasing gas molecular kinetic diameter, implying the dominance of diffusivity selectivity. The latter trend fully resonates with the suggestion by Javaid, (2005:221). Hyflon M (PFA) has a very low free volume (≈ 0), and thus diffusivity selectivity dominates. The choice of membranes with increased free volume (Halar = 1.2%, Nafion 117 = 3.77%, Udel Polysulfone = 15.5% and Teflon AF 2400 = 37%) aimed at suppressing the dominance of diffusivity selectivity and thus allow SO_2 to take advantage of its highly interactive potential to permeate preferentially through solubility selectivity. Gas properties that have a bearing on solubility in a polymeric matrix are chemical affinity with the polymer which is related to molecular polarisation, condensability and the gas molecule’s kinetic diameter (Phair, 2006:797). Shieh & Chung, (1999:2851) suggests that the solubility of a gas in a polymer is hinged on the critical temperature of the gas and the Lennard jones force constants which in-turn give a measure of gas condensability and molecular interaction respectively. Solubility of a gas in a polymer thus increases with increased condensability and increased gas-polymer molecular interactions, the gas’ critical temperature (T_c) may safely be used to estimate solubility (Park & Lee, 2008:642). It is clearly evident that SO_2 has the greatest interaction potential based on the data given in Table 4.3 and the latter discussion. SO_2 was thus expected to permeate preferentially through solubility selectivity. It must be noted however that factors inclusive of the polymer chemical structure could have a bearing on the net permeability of the gases in question (Matteucci *et al*. 2006:31). The latter was outside the scope of the present study, and the choice of polymers with increased free volume was deemed sufficient to atleast suppress diffusivity selectivity though there was a possibility of the polymer chemical structure reversing the intent.

Gas streams in need of SO_2/O_2 separation in the hybrid sulphur process contain acidic vapours, as such potential membranes should be resistant to H_2SO_4 attack.

4.1.3 CHOICE OF MEMBRANE BASED ON SCREENING EXPERIMENTS

Screening experiments were carried out in an effort to eliminate the worst performing membranes from the membranes of choice based on single component permeability values, flux values and ideal SO_2/O_2 selectivity values. Figure 4.2 gives bar chart plots of the experimental membrane permeability results plotted against pressure. It is important to note that Hyflon F experiments were carried out at pressures 1.85 bar, 2.85 bar and 3.85 bar. Table 4.4 gives a summary of the membrane screening results with ideal selectivities and Table 4.5 then gives expected gas fluxes in hypothetical 1µm thick membranes at the diverse trans-membrane pressures. Of the available membranes, it is desired to select membranes with:

1) The highest SO_2 permeability but with a low O_2 permeability
2) The highest SO_2/O_2 selectivity
3) The highest SO_2 volumetric flux but with low O_2 volumetric flux



■ 1 Bar, ▩ 2 Bar , ▨ 3 Bar, □ Literature value(References in Table 4.2). (a) Hyflon M, (b) UPS, (c) Hyflon F, (d) Nafion 117(Humidity 35%), (e) Teflon AF 2400, (f) Halar

Figure 4.2 Membrane permeability against pressure

Table 4.4 Ideal selectivity of gases against O_2

Membrane	Selectivity against O_2								
	SO_2 1 Bar	SO_2 2 Bar	SO_2 3 Bar	N_2 1 Bar	N_2 2 Bar	N_2 3 Bar	CO_2 1 Bar	CO_2 2 Bar	CO_2 3 Bar
Hyflon F	**0.74**	**0.78**	**0.99**	**0.37**	**0.30**	**0.32**	**2.21**	**2.28**	**2.49**
Halar	**-**	**-**	**16.90**	**-**	**-**	**-**	**-**	**-**	**6.76**
Nafion 117	**29.8**	**34.54**	**40.20**	**-**	**-**	**-**	**3.61**	**2.83**	**2.53**
Hyflon M	**0.83**	**0.97**	**1.11**	**-**	**-**	**0.32**	**2.46**	**2.35**	**2.43**
UPS	**46.00**	**58.47**	**314.00**			**0.22**	**6.46**	**5.20**	**5.60**
Teflon AF 2400	**1.18**	**1.05**	**1.26**	**0.45**	**0.44**	**0.46**	**2.00**	**2.03**	**2.02**

Table 4.5 Normalized gas flux values per 1 micrometer thick hypothetical film at diverse trans-membrane pressures

Membrane	Pure O_2 @ 25 ± 1˚C			Pure SO_2 @ 25 ± 1˚C			Pure N_2 @ 25 ± 1˚C			Pure CO_2 @ 25 ± 1˚C		
	Volumetric Flux ($m^3.m^{-2}hr^{-1}$) x 10^2			**Volumetric Flux ($m^3.m^{-2}hr^{-1}$) x 10^2**			**Volumetric Flux ($m^3.m^{-2}hr^{-1}$) x 10^2**			**Volumetric Flux ($m^3.m^{-2}hr^{-1}$) x 10^2**		
Hyflon F	3.85 Bar	2.85 Bar	1.85 Bar	3.85 Bar	2.85 Bar	1.85 Bar	3.85 Bar	2.85 Bar	1.85 Bar	3.85 Bar	2.85 Bar	1.85 Bar
	6.99	5.61	3.70	6.89	4.38	2.74	2.22	1.70	1.36	17.41	12.81	8.18
Halar	3 Bar	2 Bar	1 Bar	3 Bar	2 Bar	1 Bar	3 Bar	2 Bar	1 Bar	3 Bar	2 Bar	1 Bar
	0.10			1.62						0.65		
Nafion 117	3 Bar	2 Bar	1 Bar	3 Bar	2 Bar	1 Bar	3 Bar	2 Bar	1 Bar	3 Bar	2 Bar	1 Bar
	4.45	2.99	1.61	178.71	103.20	47.91				11.23	8.47	5.80
Hyflon M	3 Bar	2 Bar	1 Bar	3 Bar	2 Bar	1 Bar	3 Bar	2 Bar	1 Bar	3 Bar	2 Bar	1 Bar
	4.38	2.85	1.45	4.68	2.62	1.24	1.43			10.03	6.65	3.43
UPS	3 Bar	2 Bar	1 Bar	3 Bar	2 Bar	1 Bar	3 Bar	2 Bar	1 Bar	3 Bar	2 Bar	1 Bar
	0.81	0.55	0.28	255.59	32.11	12.92	0.18			4.56	2.85	1.81
Teflon AF 2400	3 Bar	2 Bar	1 Bar	3 Bar	2 Bar	1 Bar	3 Bar	2 Bar	1 Bar	3 Bar	2 Bar	1 Bar
	787.49	565.40	303.88	990.33	594.35	358.44	361.44	247.21	137.29	1592.39	1149.01	607.40

Figure 4.2 and Table 4.5 indicate that Teflon AF 2400, Udel Polysulfone and Nafion 117 presented the highest and desired SO_2 permeability and normalized SO_2 flux values respectively and thus could be the membranes of choice for further investigation. However, the low Teflon AF 2400 SO_2/O_2 selectivity (≈1 within the the pressure range, 1-3 Bar) presented in Table 4.4 rendered the membrane unfit for the present application. Halar presented a relatively fair SO_2/O_2 selectivity of 17 given in Table 4.4, however the low SO_2 flux of 0.0162 ($m^3.m^{-2}hr^{-1}$) at 3 bar disqualified the membrane from further investigation. Nafion 117 and Udel Polysulfone presented the highest and most desirable SO_2/O_2 ideal selectivity, SO_2 permeability and SO_2 flux values as such remained superlative membranes for further investigation.

4.2 SINGLE COMPONENT PERMEATION OF SO_2 AND O_2 IN NAFION AND UPS

A closer scrutiny to the permeability of SO_2 and O_2 in Nafion 117 and Udel Polysulfone (UPS) is presented with the purpose of identifying the effect of process parameters (pressure in the single permeation case) on permeability and normalized gas flux. Despite the presence of gas interactions in binary mixture permeation, the effect of process parameters on pure component permeation could aid optimization of the mixed gas separation.

4.2.1SINGLE PERMEATION IN UDEL POLYSULFONE

O_2 has a weaker sorbing potential compared to SO_2 based on the gas properties given in Table 4.3 (Park & Lee, 2008:642; Shieh & Chung, 1999:2851). Matteucci *et al* (2006:22) predicts that the permeability of the low sorbing components, mostly permanent gases inclusive of O_2 is either weakly or not dependant on feed pressure, which agrees closely with present experimental results (*see Figure 4.3)*. Statements by Koros & Chern, (1987:885), Park & Lee, (2008:638) , Fritzsche & Kurz, (1990:564) and Stern & Fried, (2007:1036), which highlight that supercritical gases such as N_2 and O_2 present permeability coefficients that are independent of pressure whether it be in rubbery or glassy polymers at moderate pressures are enough to validate the trend presented by the observed results.

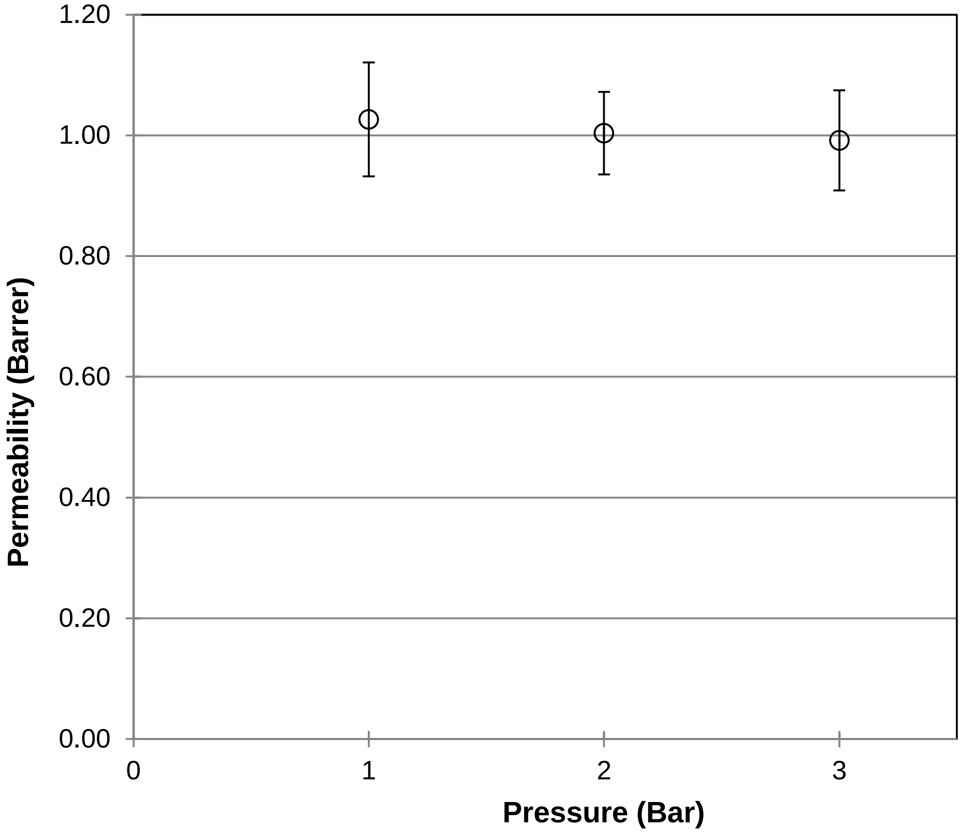


Figure 4.3 Pressure dependence of O_2 permeability in UPS

Figure 4.3 gives a plot of O_2 permeability against feed pressure and confirms the independence of O_2 permeability on feed pressure in Udel polysulfone. SO_2 however presented a pressure dependant permeability through Udel polysulfone which is evident in Figure 4.4.

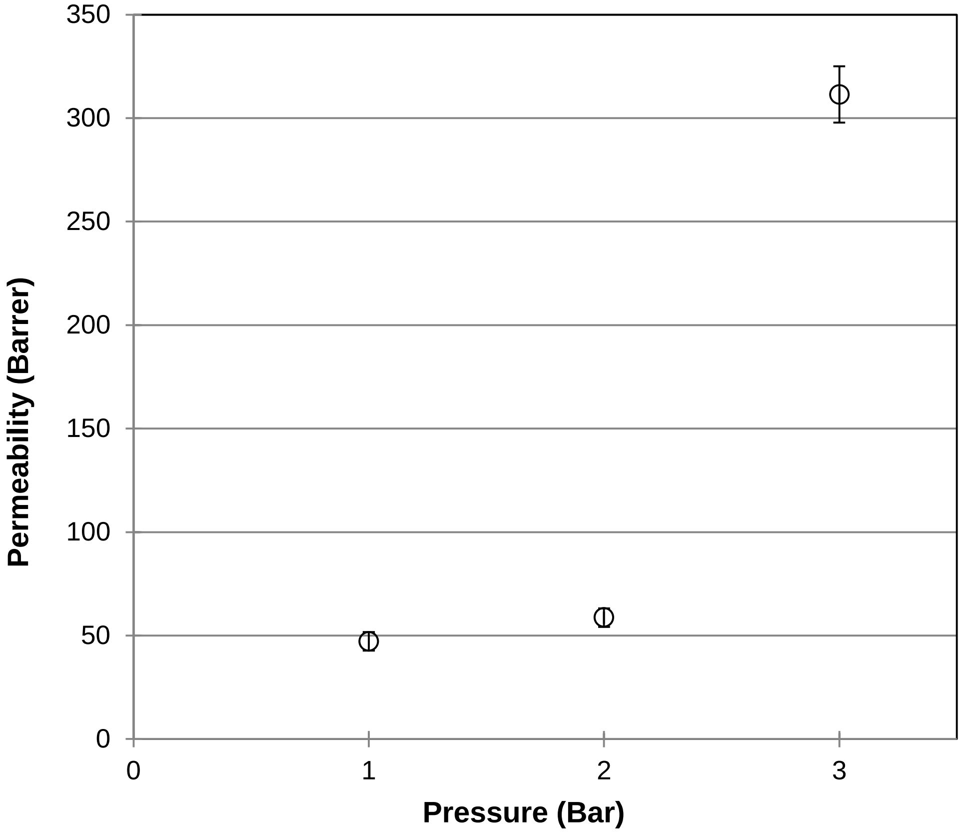


Figure 4.4 Pressure dependence of SO_2 permeability in UPS

At the feed pressure of 3 bar, a suspicious permeability point of 311.39 Barrer presents the possibility of plasticization. Plasticization initiates polymer chain spacing increments which in-turn results in increased polymer chain mobility. The net effect is an increase in diffusion and permeability coefficients (Matteucci *et al*. 2006:22). Figure 4.4 adopts a shape analogous to that presented in Figure 2.4 case (2) of Section 2.3.2 which is typical of plasticizing gases (Matteucci *et al*. 2006:22). A conclusion was thus drawn that SO_2 is highly sorbing in Udel polysulfone and has a plasticizing effect on the polymer.

An analysis of the normalized gas flux of the two gases (SO_2 and O_2) proved that the O_2 gas flux increased linearly as pressure was increased from 1 bar to 3 bar, whilst that of SO_2 increased exponentially, a phenomenon that could be of advantage in mixed gas separation, not negating though the possibility of interaction of the gases. Figure 4.5 and Figure 4.6 present the plots of O_2 and SO_2 flux against pressure respectively in Udel Polysulfone, the plot values were gotten from Table 4.5.

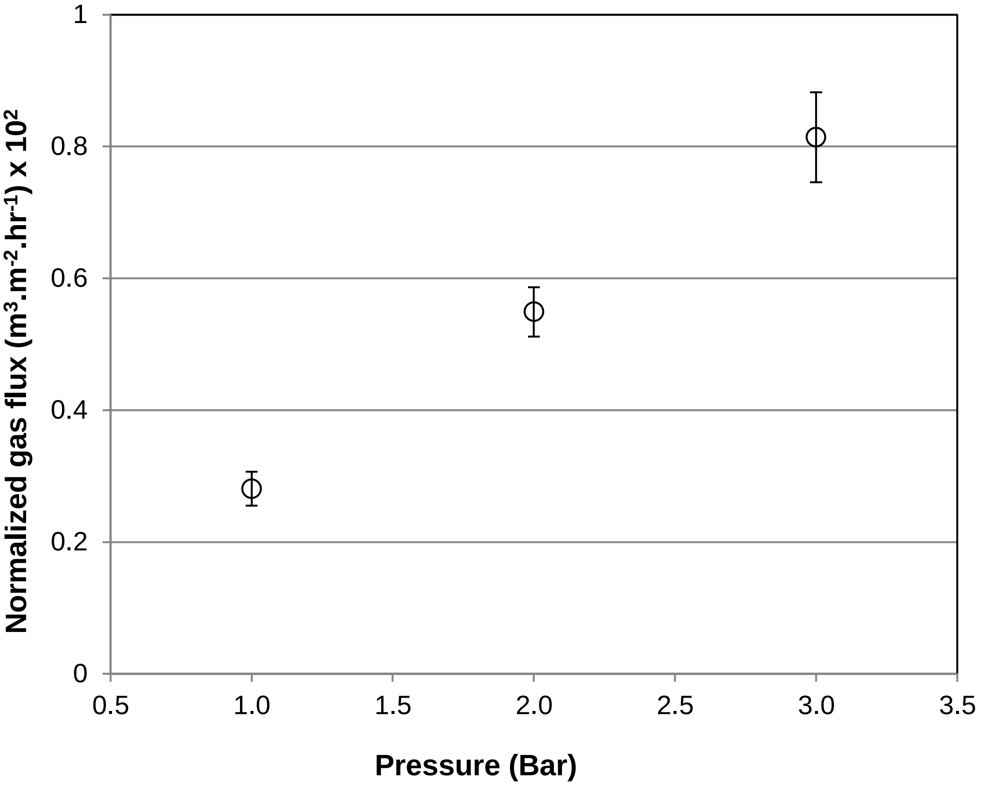


Figure 4.5 Effect of O_2 feed pressure on normalized gas flux in UPS

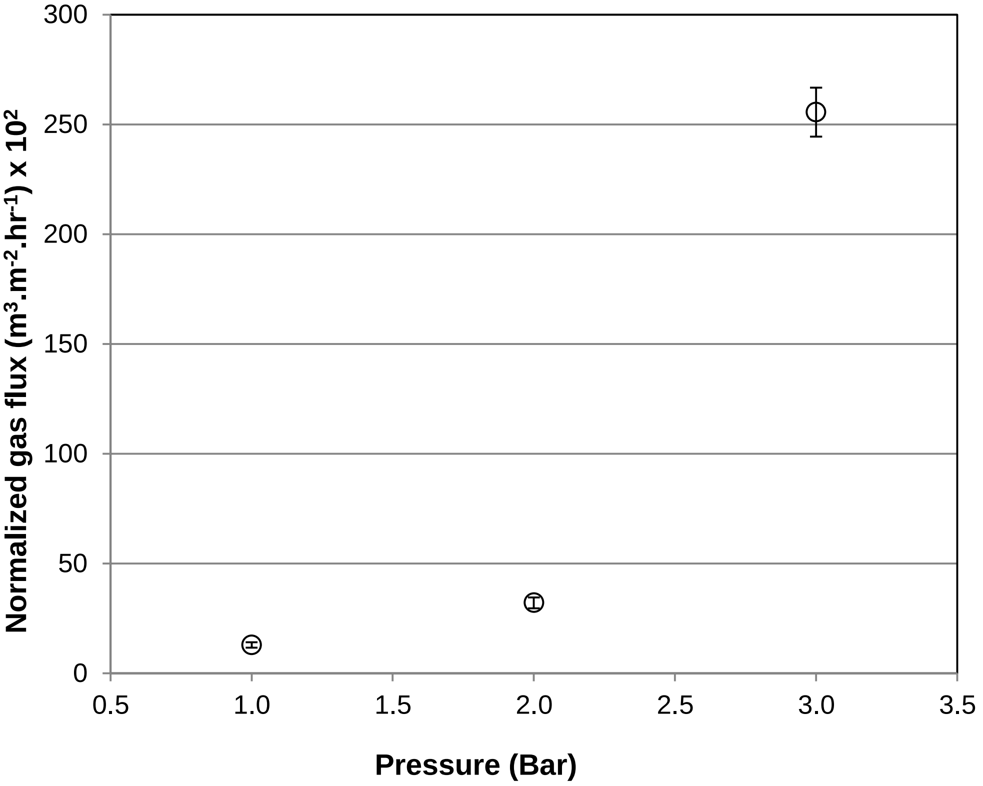


Figure 4.6 Effect of SO_2 feed pressure on normalized gas flux in UPS

4.2.2 SINGLE PERMEATION IN NAFION 117

O_2 presented a much lower gas permeability than SO_2 in Nafion 117 which was non-dependant on feed pressure and is given in Figure 4.7. The latter behavior in a similar manner with Udel Polysulfone concured with statements suggesting the independence of O_2 (permanent gas) permeability on feed pressure. SO_2 however presented a much higher pressure dependant permeability that increased with feed pressure and is given in Figure 4.9.

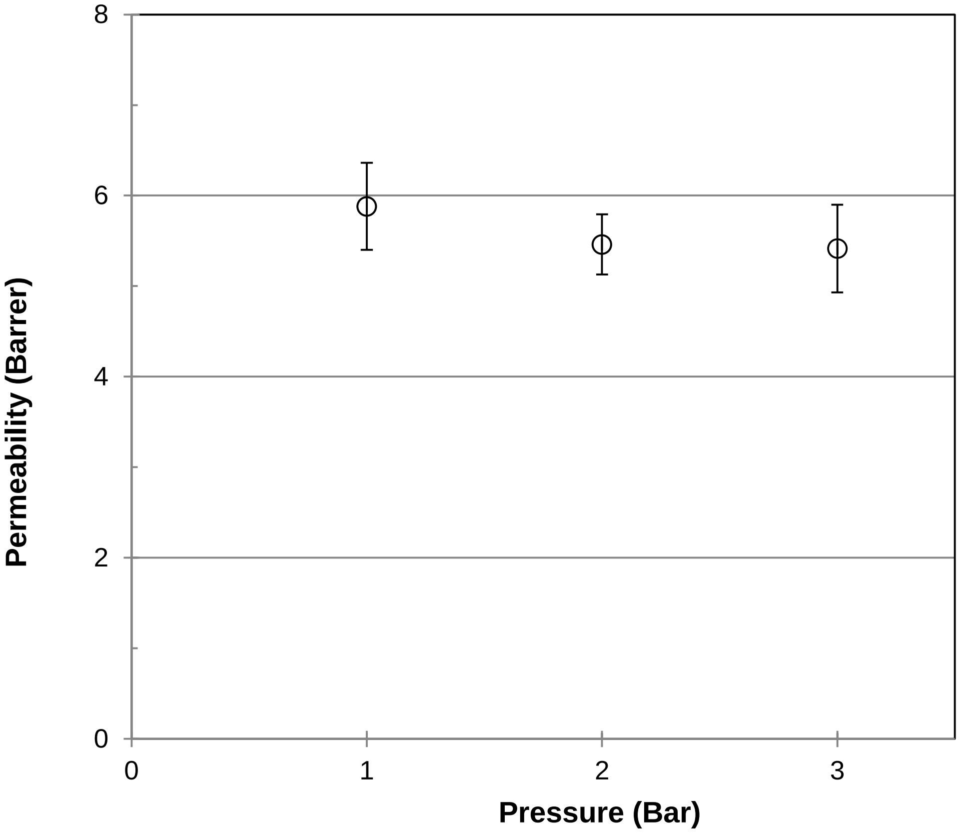


Figure 4.7 Pressure dependence of O_2 permeability in Nafion 117

With reference to Figure 4.7, the O_2 permeability values in Nafion 117 were almost identical at the three different feed pressure conditions.

Catalano, *et al*. (2012:6313) presented a study that affirmed the dependence of O_2 permeability on the relative humidity of the Nafion 117 membrane which equilibrates to the humidity of surrounding conditions (Dupont, 2009). The laboratory humidity conditions calculated from dry and wet bulb temperatures yielded a relative humidity of almost 35 %, whilst the actual weight percentage of water in the polymer at ambient conditions was

5 wt %. Figure 4.8 indicates the weight loss of a Nafion 117 sample heated to 105 ° C for 3 hours in a Mettler-Toledo Halogen moisture analyser. The weight loss was attributed to the loss of chemisorbed water which enhanced O_2 permeability in the polymer. The experimental relative humidity would be slightly less than ambient since the membrane was subjected to vacuum conditions for almost an hour thus allowing liberation of some of the chemisorbed water.

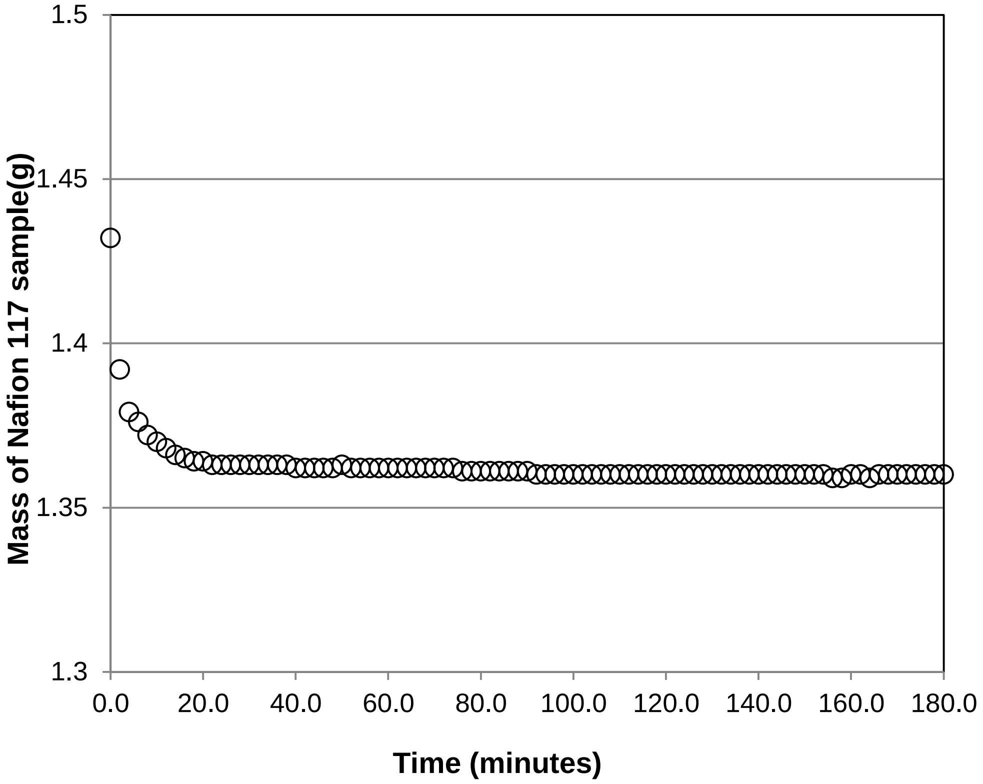


Figure 4.8 Weight loss of Nafion 117 due to water evaporation

The Nafion 117 membrane is known to be chemically stable at a temperature of 120 °C which confines any weight loss attributed to heating at 105°C to liberation of water (Orme & Stewart, 2009:512). With reference to Figure 4.8 the initial wet weight of the sample was 1.432 g and the dry weight was 1.36 g which affirmed the presence of chemisorbed water in the sample. The dependence of O_2 permeability on relative humidity ushers in more options of optimizing O_2 permeability in the polymer. Figure 4.9 presents the pressure dependence of SO_2 permeability in Nafion 117.

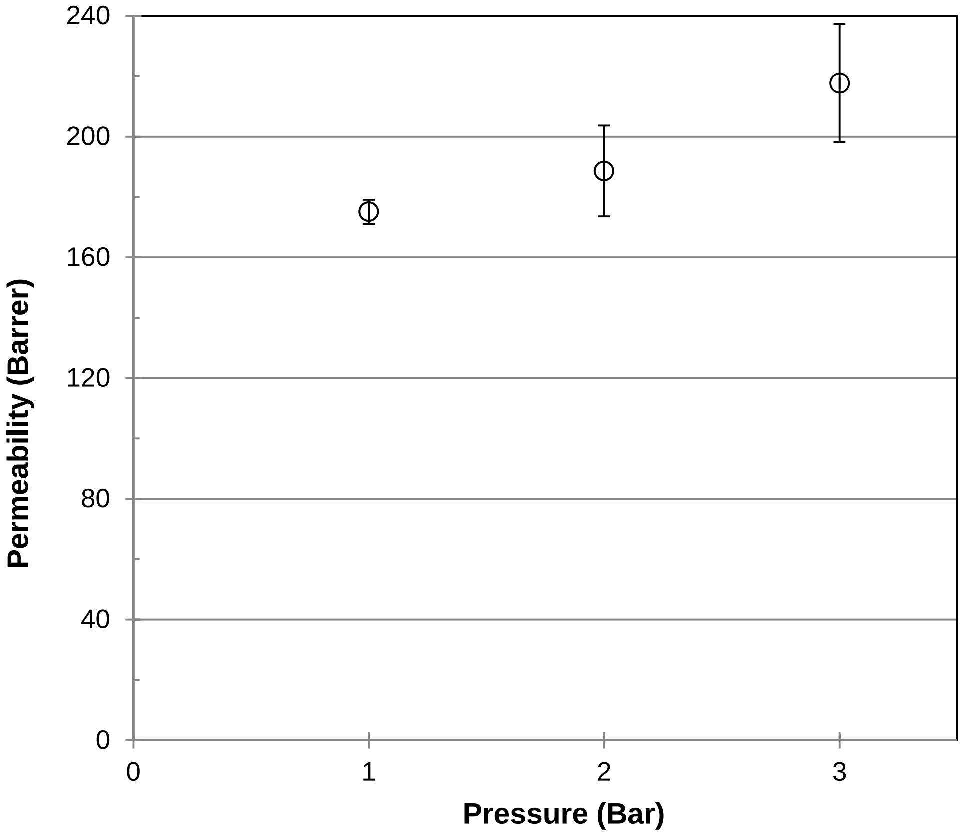


Figure 4.9 Pressure dependence of SO_2 permeability in Nafion 117

The SO_2 gas properties given in Table 4.3 justify the permeability behavior given in Figure 4.9. The much higher SO_2 critical temperature (T_c) value compared to that of O_2 affirmed the principle of increased gas solubility and thus permeability in polymers with increased gas critical temperature (T_c) (Park & Lee, 2008:642). The pressure dependence of SO_2 permeability in Nafion 117 to an extent adopted the behavior of plasticizing gases given in Figure 2.4 case (2) of Section 2.3.2 and also presented by Matteucci *et al*. (2006:22). However, the behavior presented by SO_2 in Nafion 117 was less pronounced, probably indicating weaker plasticization in contrast to SO_2 permeability in Udel Polysulfone.

Figure 4.10 presents the normalized gas flux of O_2 (flux based on hypothetical 1 µm thick films) through Nafion 117.

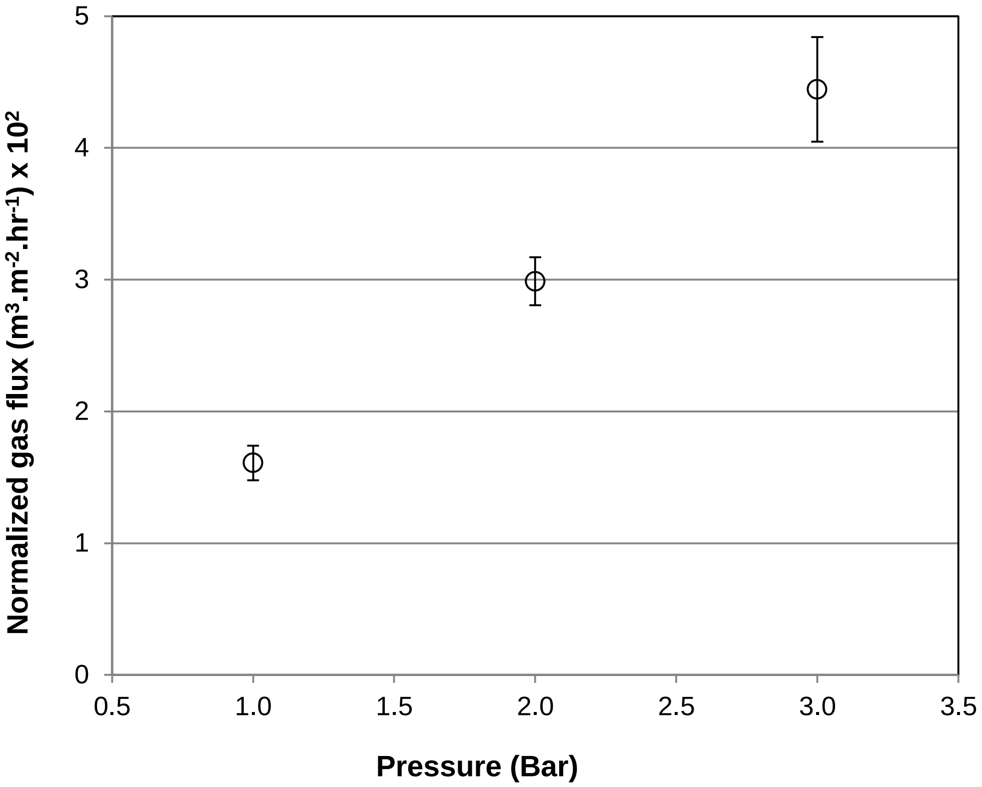


Figure 4.10 Effect of O_2 feed pressure on normalized gas flux through Nafion 117

O_2 presented an almost linear relationship between the normalized gas flux (flux based on hypothetical 1 µm thick films) through the Nafion 117 membrane and the feed pressure. The SO_2 flux behavior is given in Figure 4.11.

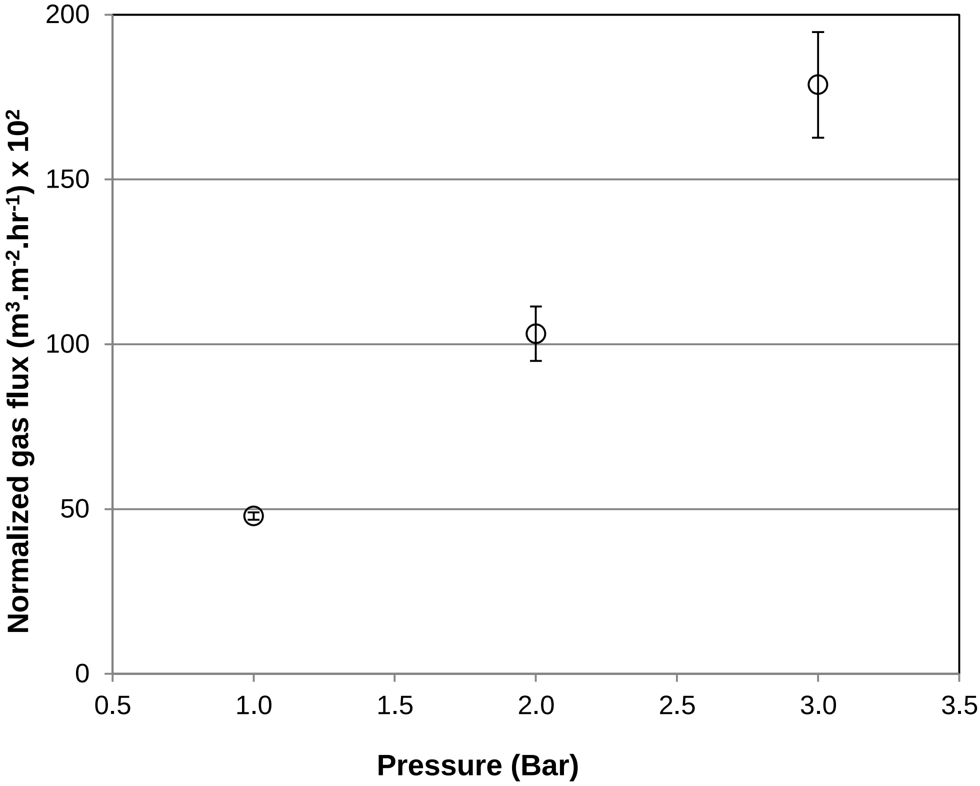


Figure 4.11 Effect of SO_2 feed pressure on normalized gas flux through Nafion117

The SO_2 normalized gas flux (flux based on hypothetical 1 µm thick films) through Nafion 117 also presented a linear relationship with feed pressure in contrast to the exponential behavior presented in Udel Polysulfone.

4.2.3 COMPARISON OF THE SO_2 AND O_2 PERMEATION IN THE NAFION 117 AND UPS

Matteucci *et al* (2006:12) state that the presence of a particular gas in a mixture can influence the transport of other gases present. As a result, the pure gas or ideal selectivity is rendered as a crude estimate of the real selectivity. However, the latter is almost inapplicable in rubbery polymers where the ideal selectivity is a good approximation of the real selectivity (Matteucci *et al*. 2006:12). A great need thus arises to conduct binary permeation experiments in light of the fact that both Nafion 117 and Udel Polysulfone are glassy polymers (Tg values given in Table 3.2 of Section 3.1). Figure 4.12 presents a comparison of ideal SO_2/O_2 selectivities of the two membranes.

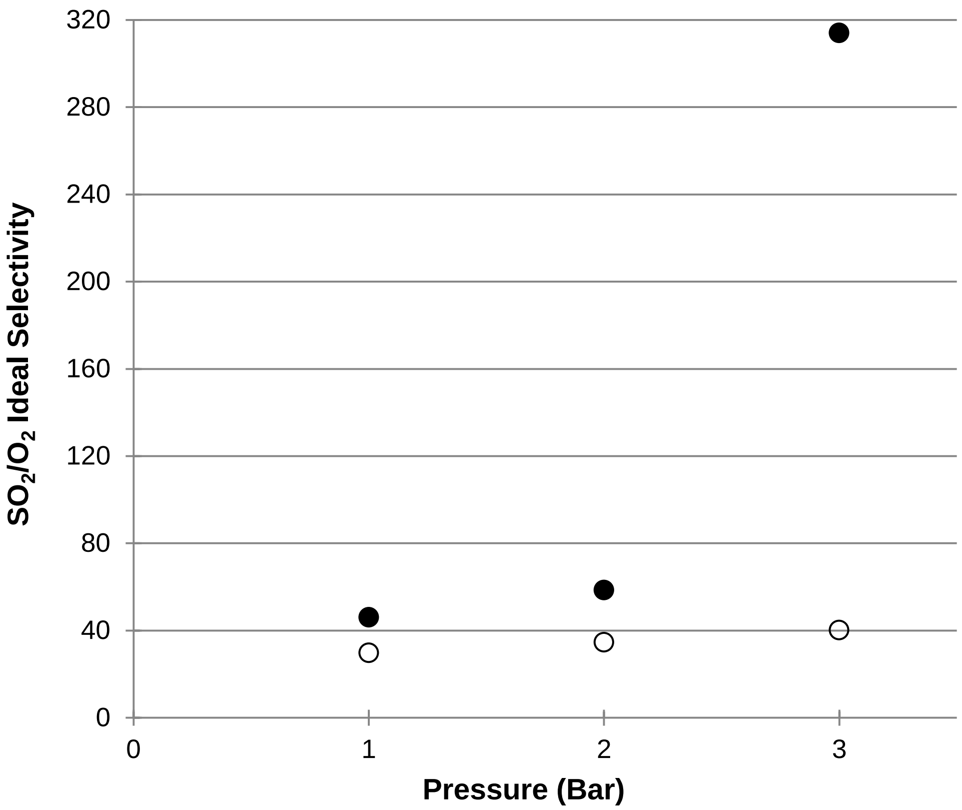


Figure 4.12 Pressure dependence of SO_2/O_2 ideal selectivity in Nafion 117 ○ and Udel Polysulfone ●

Judging the membranes' performance from ideal selectivity given in Figure 4.12, one may declare Udel polysulfone to have an upper hand over Nafion 117 which may not necessarily be the case. The SO_2 plasticization phenomena in Udel polysulfone could allow increased permeability of O_2 in the binary mixture and thus reduced SO_2/O_2 selectivity (Matteucci *et al* 2006:40). Nafion 117 presented generally superior SO_2 gas fluxes over Udel Polysulfone based on hypothetical 1 µm thick membranes at feed pressures of 1 bar and 2 bar. An exception however was observed at the 3 Bar SO_2 pressure point where a higher SO_2 flux was observed in Udel Polysulfone and plasticization was suspected. Nafion 117 could thus be dearer of the two membranes, however only the binary gas experiments would tell.

4.3 BINARY PERMEATION OF SO_2/O_2 GAS MIXTURES IN NAFION AND UPS

Binary permeation results of the mixtures (25 wt% SO_2: 75wt % O_2), (50 wt% SO_2: 50wt % O_2) and (75 wt% SO_2: 25 wt % O_2) in Nafion 117 and Udel Polysulfone at a temperarure range of 15 °C to 55°C and upstream SO_2 partial pressure range of 1.0 to 2.4 bar are presented in Section 4.3.

The presence of several gas constituents in a gas mixture often offer significant contribution to the transport characteristics of each other through a polymer especially in systems involving condensable and highly sorbing gases (Matteucci *et al*. 2006:3; Matteucci *et al*. 2006:40). Envisaged competition of gas molecules for sorption sites on the polymer matrix, and general increased diffusion of all gas molecules attributed to plasticization by a condensable molecule is thought to occur in mixed gas systems (Matteucci *et al*. 2006:40). As such relying on the ideal selectivity found from single permeation experiments may be dire. Binary permeation experiments were thus performed based on the background of the poor reliability of single component permeation data in predicting binary permeation data.

It is important to note that the membrane thicknesses employed in the present study (Udel Polysulfone = 75 µm, Nafion 117 = 177 µm) were used for the purposes of conducting the research through determining important coefficients and characteristics of the polymers. Commercial membrane gas separation applications employ membranes as thin as 1 µm or less (Baker, 2002:1394). Based on the former background, flux considerations have been based on a hypothetical 1 µm thick membrane for both Nafion 117 and Udel Polysulfone. Udel Polysulfone has been successfully extruded in thicknesses less than 0.1 µm (Wang *et al*. 2002:250) , however thicknesses of 1 µm or less for nafion/perfluorosulfonic acid based membranes are unknown of.

4.3.1 BINARY PERMEATION IN NAFION 117

Nafion 117 also known to be a perfluorosulfonic acid based polymer presented both temperature and pressure dependant SO_2/O_2 real selectivities. SO_2 being the faster gas, its composition in the permeate chamber generally decreased with increasing temperature and increased with increasing upstream SO_2 partial pressure. Figures 4.13 (a), (b) and (c) present the temperature dependence of both SO_2 permeate composition and SO_2/O_2 selectivity at diverse temperatures and a SO_2 trans-membrane partial pressure of 1.1 bar ± 0.1. Figures 4.14 (a), (b) and (c) present the temperature dependence of both SO_2 and O_2 pseudo permeability ($\prod_{SO_2}$ and $\prod_{O_2}$) at diverse temperatures and at a SO_2 trans-membrane partial pressure of 1.1 bar ± 0.1. Finally, Figures 4.15 (a), (b) and (c) present the effect of temperature on the molar fluxes of the two gases also at a SO_2 trans-membrane partial pressure of 1. bar ± 0.1. The respective error bars are also plotted on the same chart.

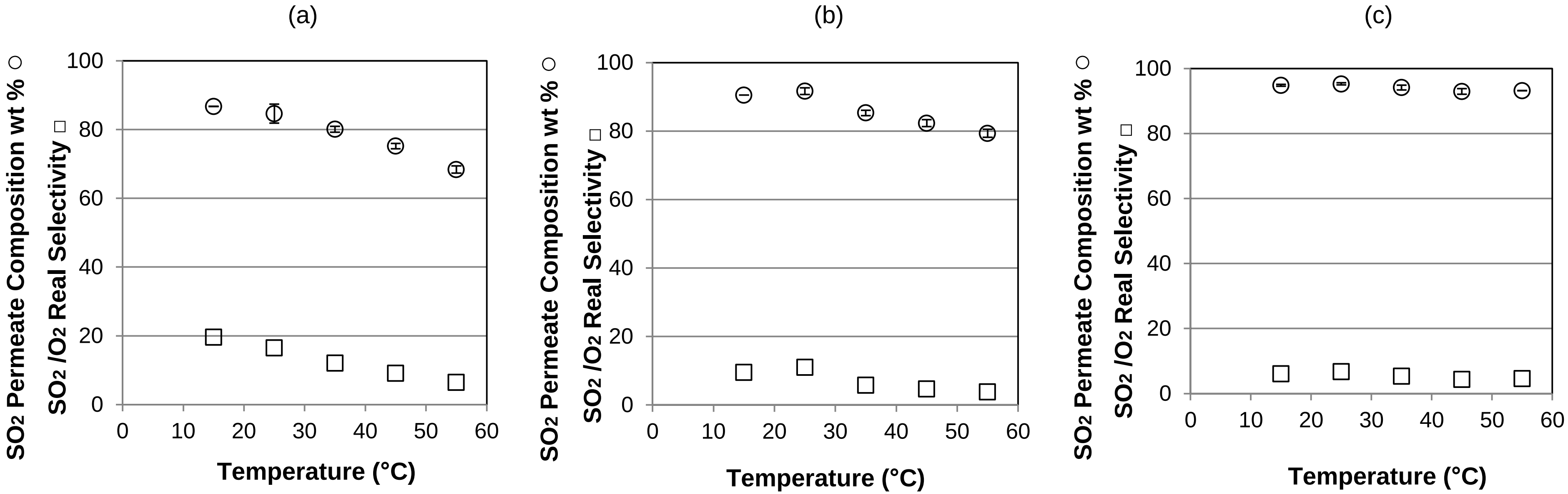


Figure 4.13 Effect of temperature on SO_2 permeate composition & SO_2/O_2 real selectivity in Nafion 117 at Δp_{SO2} of 1.1 bar ± 0.1 with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 (c) 75 wt % feed SO_2

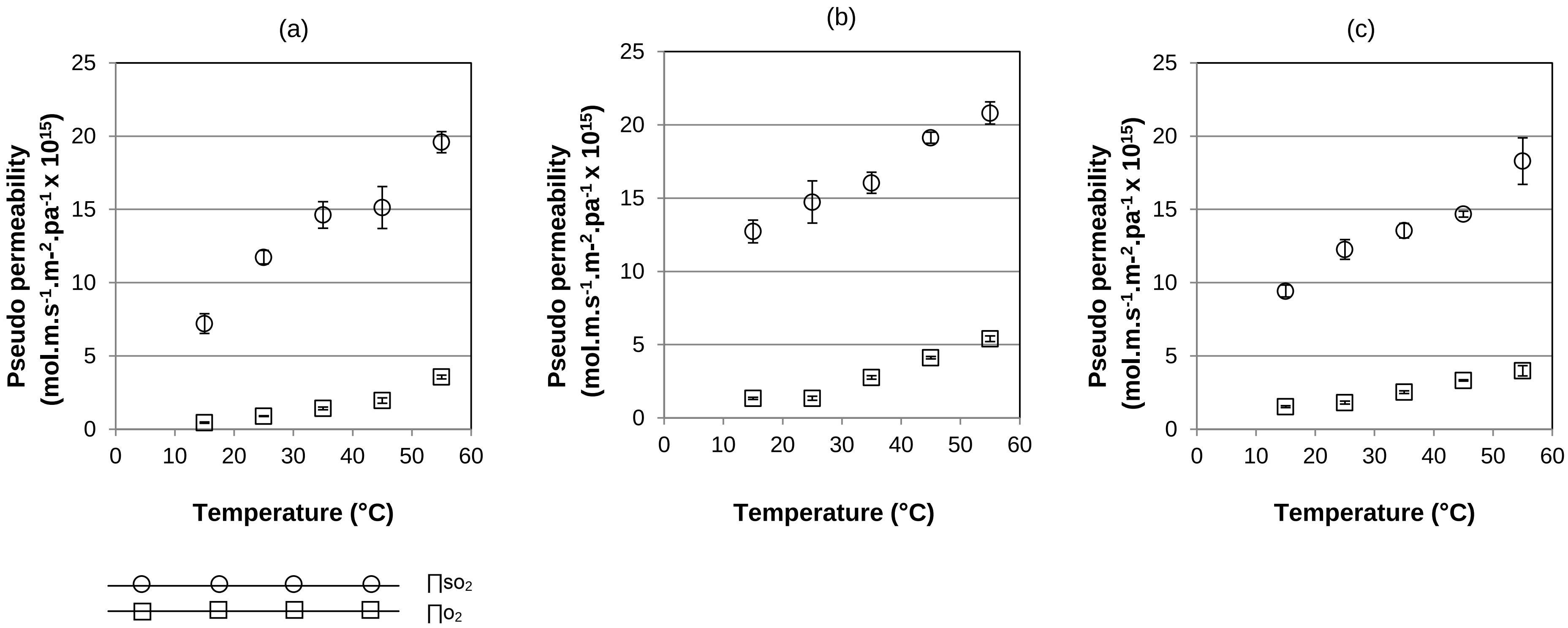


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Figure 4.14 Effect of temperature on SO_2 and O_2 pseudo permeability in Nafion 117 at Δp_{SO2} of 1.1 bar ± 0.1 with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 (c) 75 wt % feed SO_2

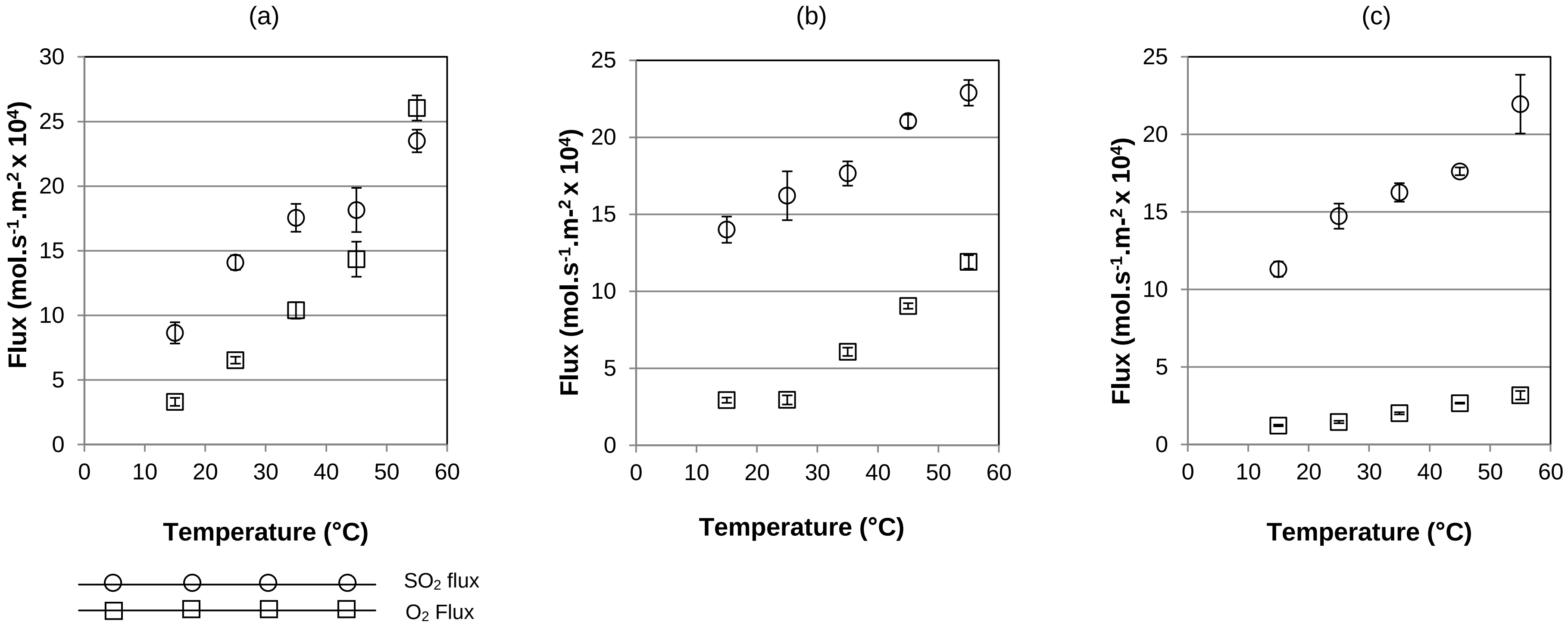


Figure 4.15 Effect of temperature on SO_2 and O_2 molar flux in Nafion 117 at Δp_{SO2} of 1.1 bar ± 0.1 with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 (c) 75 wt % feed SO_2

The SO_2 gas separation behavior presented by Nafion 117 in Figures 4.13 (a), (b) and (c) is analogous to that presented by the sulfone modified polyvinylidene fluoride membranes studied by Zavaleta & McCandless, (1976:333). Zavaleta & McCandless, (1976:333) studied the separation of SO_2 from mixtures with N_2 (a permanent gas just like O_2, Victor *et al*. 2008:934), and stated that best separation was observed at low process temperatures (Zavaleta & McCandless, 1976:333; Baker, 2008:560). The similar behavior could have been attributed to the presence of sulfone in both polymers, Nafion 117 (Perfluorosulfonic acid membrane) and the Sulfone modified polyvinylidene fluoride membranes. Low process temperatures enhance the solubility of condensable gases in polymers. Based on Equation 2.8 of Section 2.3, the latter statement was fully explained by Dhingra, (1997:41) who stated that the enthalpy of solution ΔH_s is mathematically presented thus.

$$\Delta H_s = \Delta H_{condensation} + \Delta H_{mixing} \qquad (4.1)$$

Where:

ΔH_s is the enthalpy of sorption

$\Delta H_{condensation}$ is the enthalpy of condensation of the gas molecule in the polymer

ΔH_{mixing} is the enthalpy required to create a molecular scale gap for the gas molecule in the polymer

$$S = S_o \exp\left[\frac{-\Delta H_s}{RT}\right] \qquad (2.8)$$

Where:

S is the solubility,

ΔH_s is the enthalpy of solution of the sorbate

S_o is a pre-exponent factor

R is the molar gas constant

T is the temperature in Kelvin

In the present study it was envisioned that the low condensing nature of O_2 (vapor pressure of 1481.86 Bar at 15°C (Poling *et al.* 2008:2-59)) rendered the condensation term less dominant and the weak gas-polymer interactions typical of permanent or non-critical gases such as O_2 made the mixing enthalpy large and positive. As such the overall O_2 sorption enthalpy turned out to be large and positive and thus translated to decreased solubility with decreased temperature in accordance to Equation 2.8. SO_2 (vapor pressure of 2.81 bar at 15°C (Poling *et al*. 2008:2-60)) on the contrary is much more condensable than O_2 as such the condensation term may be deemed to have been highly negative and dominant, translating to an overall large negative enthalpy of sorption. The overall SO_2 solubility in the polymer thus increased with decreasing temperature in accordance to Equation 2.8.

Increased SO_2 solubility with decreasing temperature then led to increased SO_2 permeability since permeability is a function directly proportional to solubility. The latter facts then explained the increase of SO_2 composition in the permeate chamber with decreasing temperature.

In addition to the given explanation, one might present an argument that diffusivity, a term directly proportional to permeability decreases with temperature, as such a decrease in SO_2 permeability should have been expected with decreasing temperature. However Equation 2.1 of Section 2.2.2 presents permeability as a product of diffusivity and solubility, and the only explanation of an increase in SO_2 permeability despite any decrease in diffusivity is the dominance of the solubility term that rendered the SO_2 permeation process in the present case, a solubility controlled permeation process.

Re-focussing on Figure 4.13, the SO_2 permeate composition generally increased as SO_2 composition in the feed was increased which is simple logic. The SO_2 permeate composition in Figure 4.13 (c) which had the highest SO_2 feed composition (75 wt %) was seemingly unaffected by temperature. However a good explanation to the phenomenon is that the polymer probably got readily saturated with SO_2 in the gas mixture that had a high SO_2 molar density (75 wt% = 60 mol%) such that any further temperature decrease would not contribute to increased SO_2 sorption in the temperature range considered. The high SO_2 molar density (75 wt% = 60 mol%) compared to the other gas mixtures (50 wt% = 33.3 mol%) and (25 wt% = 14.1 mol%) meant that the probability of SO_2 getting into contact with the polymer was much higher and thus the prevalence of SO_2 sorption was higher too.

A similar explanation of the SO_2/O_2 selectivity behaviour with temperature was expected since the selectivity equation is hinged on the compositions of the gases both in the feed and permeate chambers. Equation 4.2 presents the selectivity relation.

$$\alpha_{SO2/O2} = y(1-x)/x(1-y) \quad (4.2)$$

where: $\alpha_{SO2/O2}$ is the SO_2/O_2 selectivity

y, is the permeate mass fraction of SO_2

x, is the upstream mass fraction of SO_2

Figure 4.14 shows that the SO_2 pseudo permeability seemingly increased much more than that of O_2 with temperature, but in actuality, from 15°C to 55°C, SO_2 permeability in Figure 4.14 (a) increased almost 3 fold whilst that of O_2 increased almost 9 fold. It was envisaged that temperature had an effect of softening the rigidity of polymer chains which translated to increased gas molecule transport through the polymer. The latter facts thus explain the rapid increase in both SO_2 and O_2 fluxes with temperature observed in Figure 4.15 (a). The flux values presented in Figure 4.15 are in fact expected fluxes in films with a hypothetical thickness of 1 µm. It is important to note that in commercial gas separation applications, typical thicknesses in use are less than 0.5 µm and some also go below 0.1 µm (Baker, 2002:1394). The use of the normalized flux (flux based on 1 µm thickness) also allowed for comparison of the flux observed in the two membranes that were of differing thicknesses in the current study.

Figures 4.16 (a) , (b) and (c) present the effect of SO_2 feed partial pressure on SO_2 permeate composition and SO_2/O_2 real selectivity at 25°C in Nafion 117. Figures 4.17 (a), (b) and (c) present the effect of total trans-membrane pressure on both SO_2 and O_2 pseudo permeability and Figures 4.18 (a), (b) and (c) present the effect of total trans-membrane pressure on SO_2 and O_2 molar flux (flux based on hypothetical 1 µm thick films) in Nafion 117. The respective error bars are plotted on the same chart.

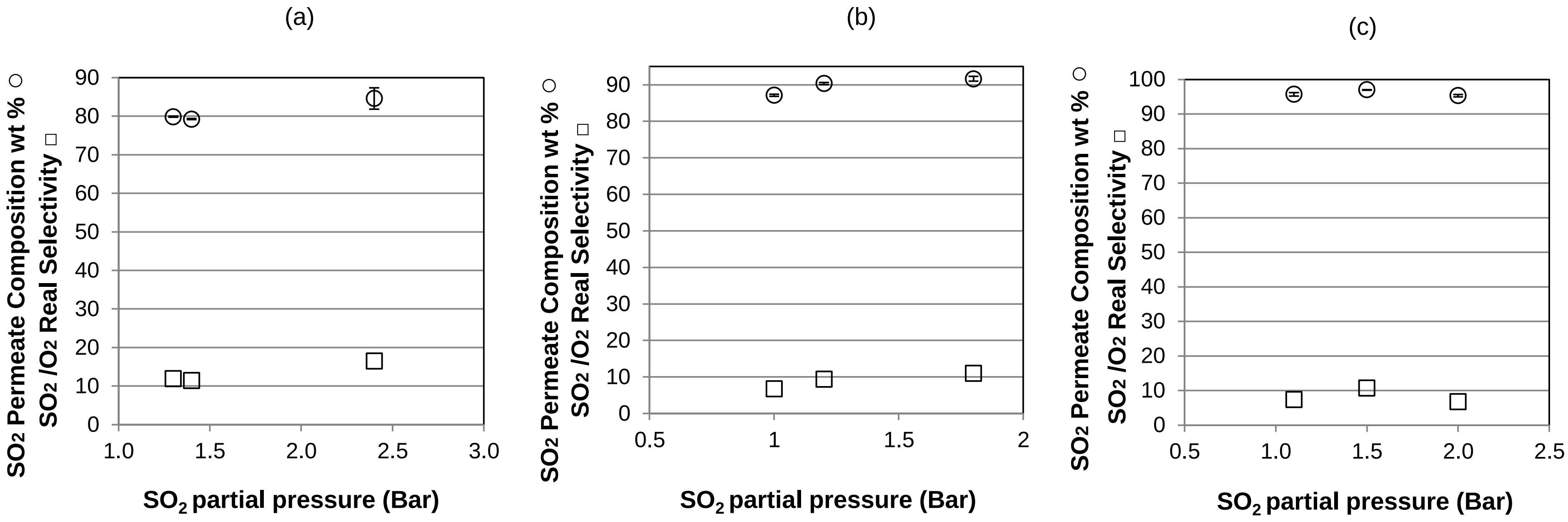


Figure 4.16 Effect of SO_2 feed partial pressure on SO_2 permeate composition in Nafion 117 at 25°C with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 and (c) 75 wt % feed SO_2

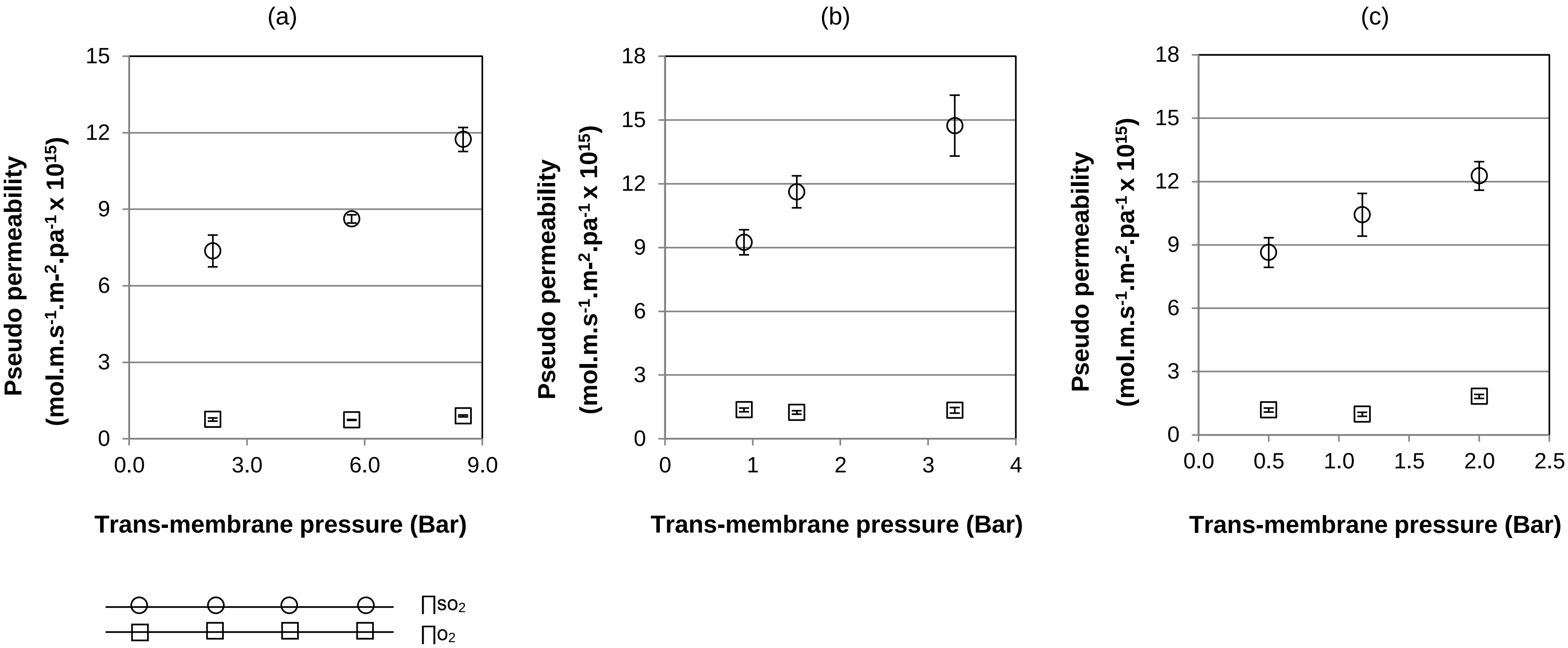


Figure 4.17 Effect of total trans-membrane pressure on SO_2 and O_2 pseudo permeability in Nafion 117 at 25°C with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 (c) 75 wt % feed SO_2

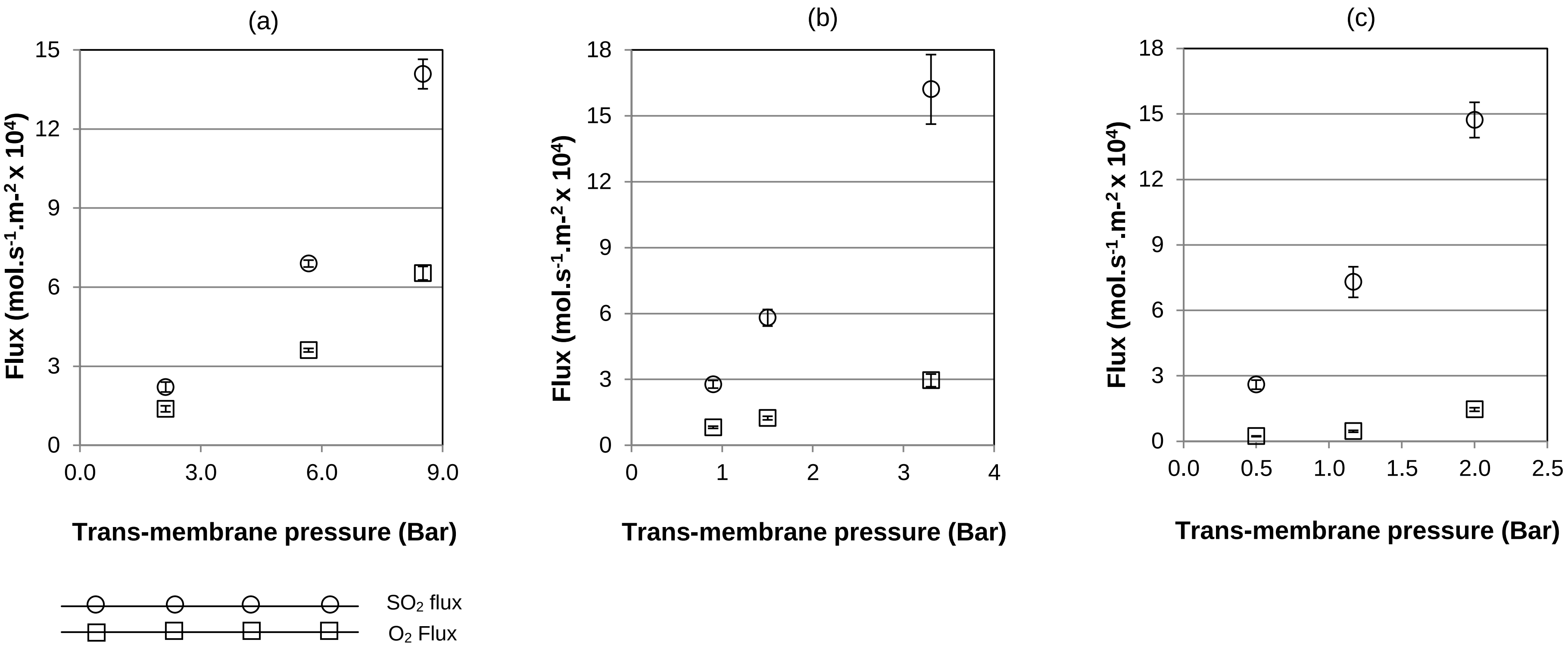


Figure 4.18 Effect of total trans-membrane pressure on SO_2 and O_2 molar flux in Nafion 117 at 25°C with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 (c) 75 wt % feed SO_2

Figure 4.16 shows that the effect of feed SO_2 partial pressure on SO_2 permeate composition in the SO_2 feed partial pressure range of 1.1 to 2.4 bar was not profound at the 3 different compositions. Though not profound the slight increase in SO_2 permeate composition noted on both 25 wt% SO_2 and 50 wt % SO_2 feed cases could not be negated. An increase in SO_2 feed partial pressure implied an increase in the quantity of SO_2 in the feed gas mixture as such the amount of SO_2 sorbed in the polymer was bound to increase. The latter statement resonates with the Dual mode sorption model that postulates that gas solubility increases in glassy polymers with an increase in pressure (Matteucci *et al*. 2006:40). The increased SO_2 solubility translated to increased SO_2 in the permeate. Despite the corresponding increase in O_2 partial pressure in the feed the low O_2 sorption potential was deemed insufficient to significantly increase O_2 in the permeate (The latter is also discussed in Section 4.1.2). At the high SO_2 feed composition of 75 wt%, it may be thought that the polymer was already saturated by SO_2 gas at the low partial pressure of 1.1 bar such that increasing the SO_2 partial pressure to 2 bar contributed insignificantly to the amount of already saturated sorbed SO_2 in the polymer. Adding further discussion to the latter statement, the high SO_2 molar density of the gas mixture (75 wt% = 60 mol%) as was presented earlier in Section 4.3.1, could have been responsible for readily saturating the polymer at the low SO_2 partial pressure of 1.1 bar.

Shown in Figures 4.17 (a), (b) and (c), the pseudo permeability of both SO_2 and O_2 increased with increasing trans-membrane pressure, the latter fact is consistent with the behaviour observed with SO_2 in the single permeation experiments. SO_2 presented a pressure dependent permeability in Nafion 117, however O_2 permeability in the single permeation experiments was independent of pressure. A valid explanation of the differing behaviours of O_2 in single and binary permeation experiments was the envisaged polymer-gas molecule interactions ushered in by SO_2 which enhanced O_2 transport in the binary permeation case.

The general increase in flux for both SO_2 and O_2 observed with increasing trans-membrane pressure in Figure 4.18 was attributed to the fact that, pressure is the driving force for permeability as such an increase in pressure would translate to increased flux in both gases.

4.3.2 BINARY PERMEATION IN UDEL POLYSULFONE

Udel Polysulfone, a glassy polymer presented a SO_2/O_2 separation behaviour similar to that which was presented by Nafion 117. Both temperature and pressure influenced the SO_2 composition in the permeate. Figures 4.19 (a), (b) and (c) present the temperature dependence of both SO_2 permeate composition and SO_2/O_2 selectivity at diverse temperatures (15°C to 55°C) and constant trans-membrane SO_2 partial pressure (1.0 bar ± 0.2) in Udel Polysulfone. Figures 4.20 (a), (b) and (c) present the effect of temperature on pseudo permeability of both SO_2 and O_2 in Udel Polysulfone. Figures 4.21 (a), (b) and (c) then present the effect of temperature on the molar fluxes (fluxes based on hypothetical 1 µm thick films) of both gases in Udel Polysulfone. The respective error bars are also plotted on the same chart.

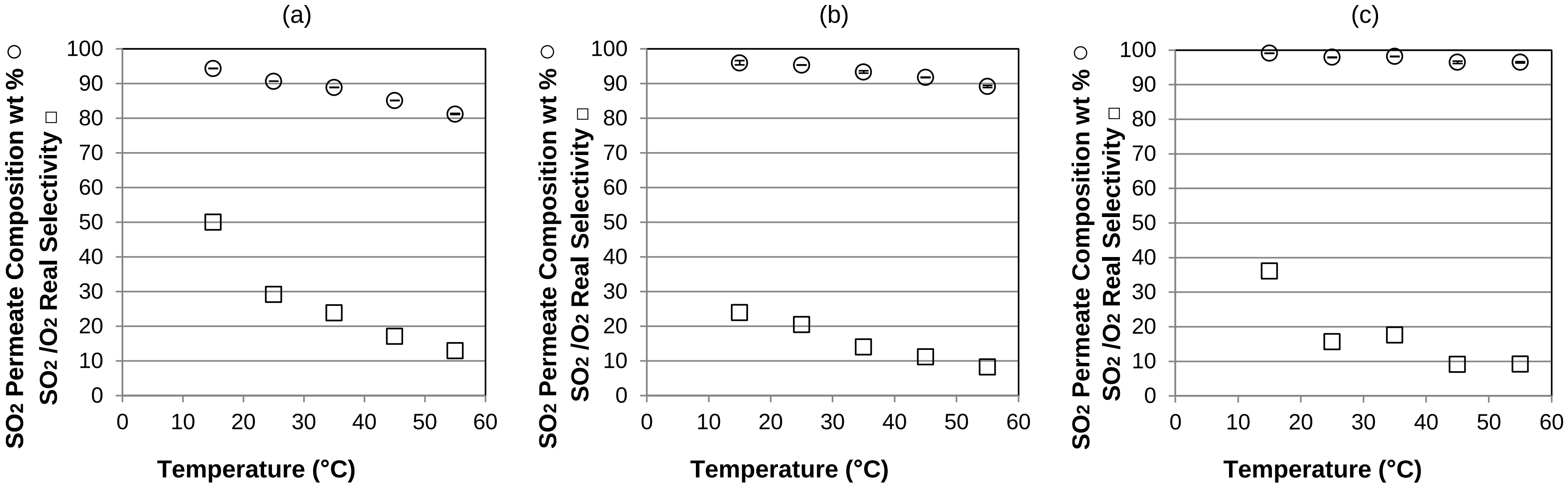


Figure 4.19 Effect of temperature on SO_2 permeate composition and SO_2/O_2 real selectivity in Udel Polysulfone at Δp_{SO2} 1 bar ± 0.2 with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 (c) 75 wt % feed SO_2

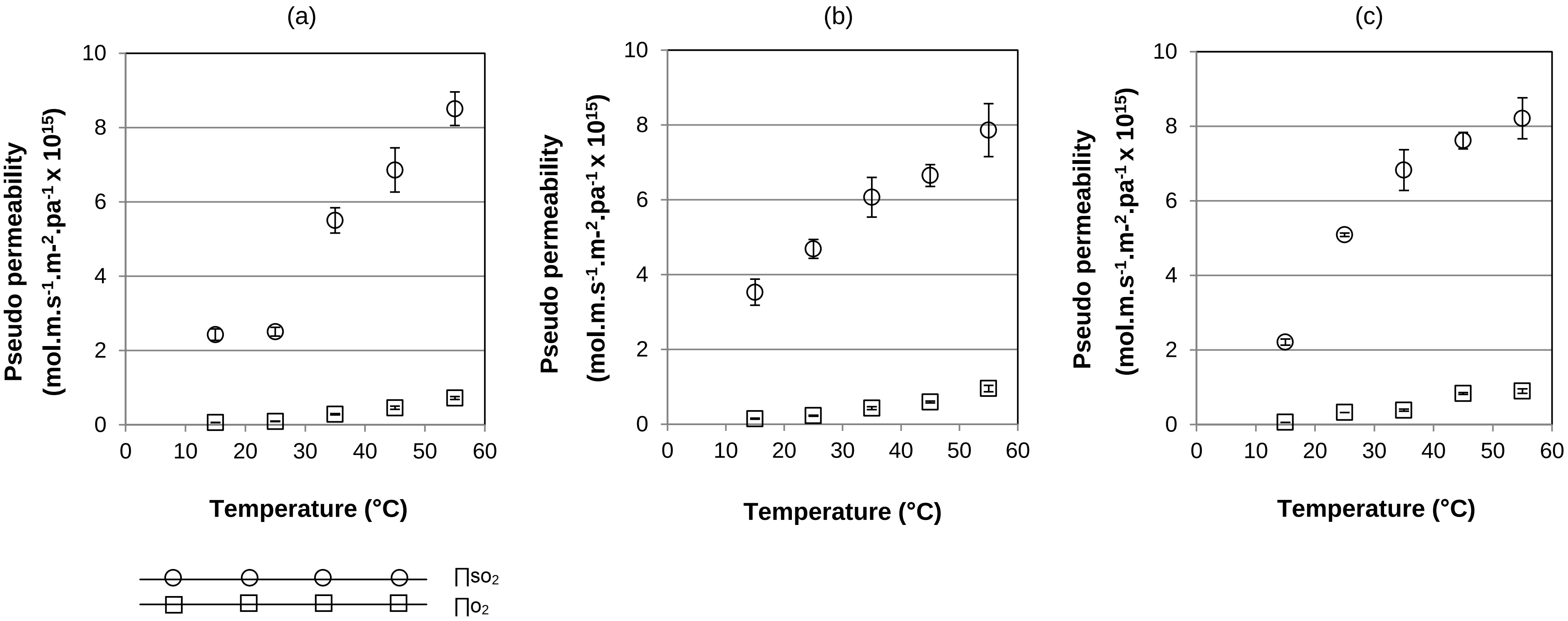


Figure 4.20 Effect of temperature on SO_2 and O_2 pseudo permeability in Udel Polysulfone at Δp_{SO2} 1 bar ± 0.2 with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 (c) 75 wt % feed SO_2

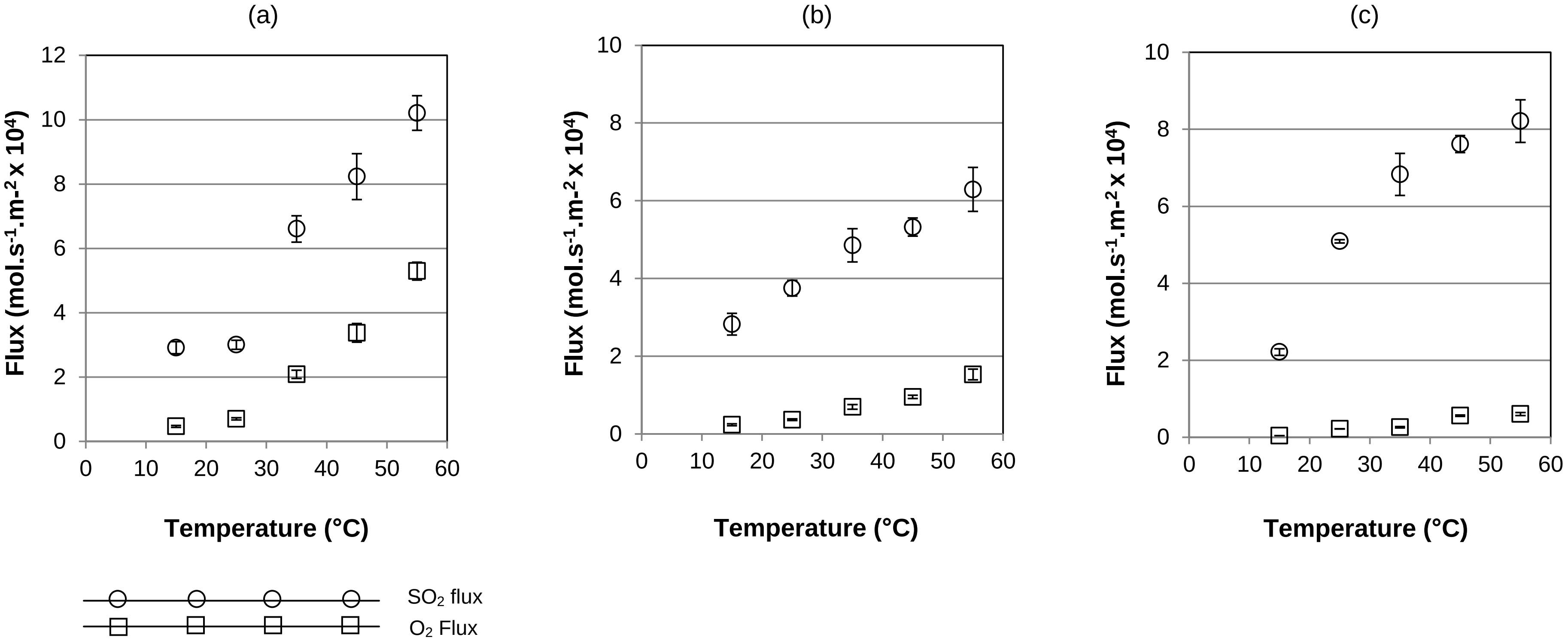


Figure 4.21 Effect of temperature on SO_2 and O_2 molar flux in Udel Polysulfone at Δp_{SO2} 1 bar ± 0.2 with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 (c) 75 wt % feed SO_2

For the same reason of increased SO_2 in the permeate with decreased temperature in Nafion 117, the SO_2 permeate composition for Udel Polysulfone increased with decreasing temperature. The explanation is given in Section 4.3.1 and needs not be repeated. However, there could be a possibility of the presence of differing transport mechanisms attributed to the differing polymer structures in the membranes. The SO_2 and O_2 fluxes generally increased with increasing temperature in Udel Polysulfone as was observed with Nafion 117. The latter observation was attributed to softening of polymer chains by heat which translated to increased polymer chain mobility and thus increased gas transport through the polymer. As the SO_2 feed composition was increased from 25 wt% to 75 wt% in Figures 4.21 (a), (b) and (c), the O_2 partial pressure in the feed decreased as such translated to decreased O_2 flux with decreased O_2 in the feed.

Figures 4.22 (a) , (b) and (c) present the effect of SO_2 feed partial pressure on SO_2 permeate composition and SO_2/O_2 real selectivity at 25 ° C in Udel Polysulfone. Figures 4.23 (a), (b) and (c) present the effect of total trans-membrane pressure on the SO_2 and O_2 pseudo permeabilities. Figures 4.24 (a), (b) and (c) present the effect of total trans-membrane pressure on SO_2 and O_2 fluxes (fluxes based on hypothetical 1 µm thick films) in Udel Polysulfone with the respective error bars plotted on the same graph.

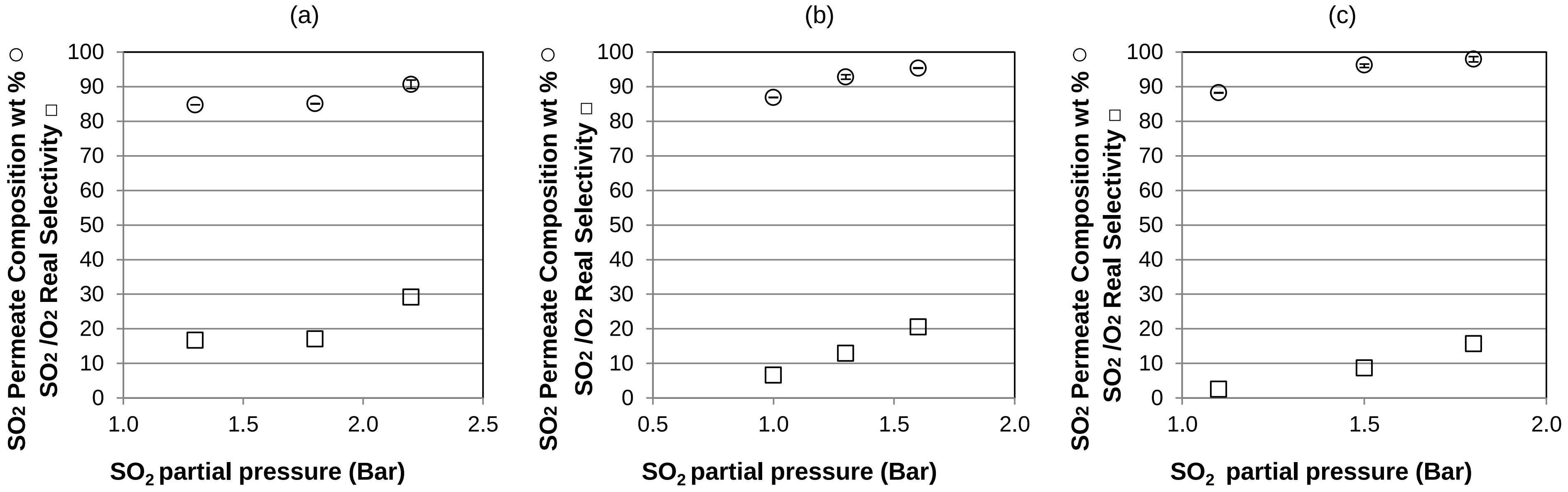


Figure 4.22 Effect of SO_2 feed partial pressure on SO_2 permeate composition and SO_2/O_2 real selectivity in Udel Polysulfone at 25°C with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 (c) 75 wt % feed SO_2

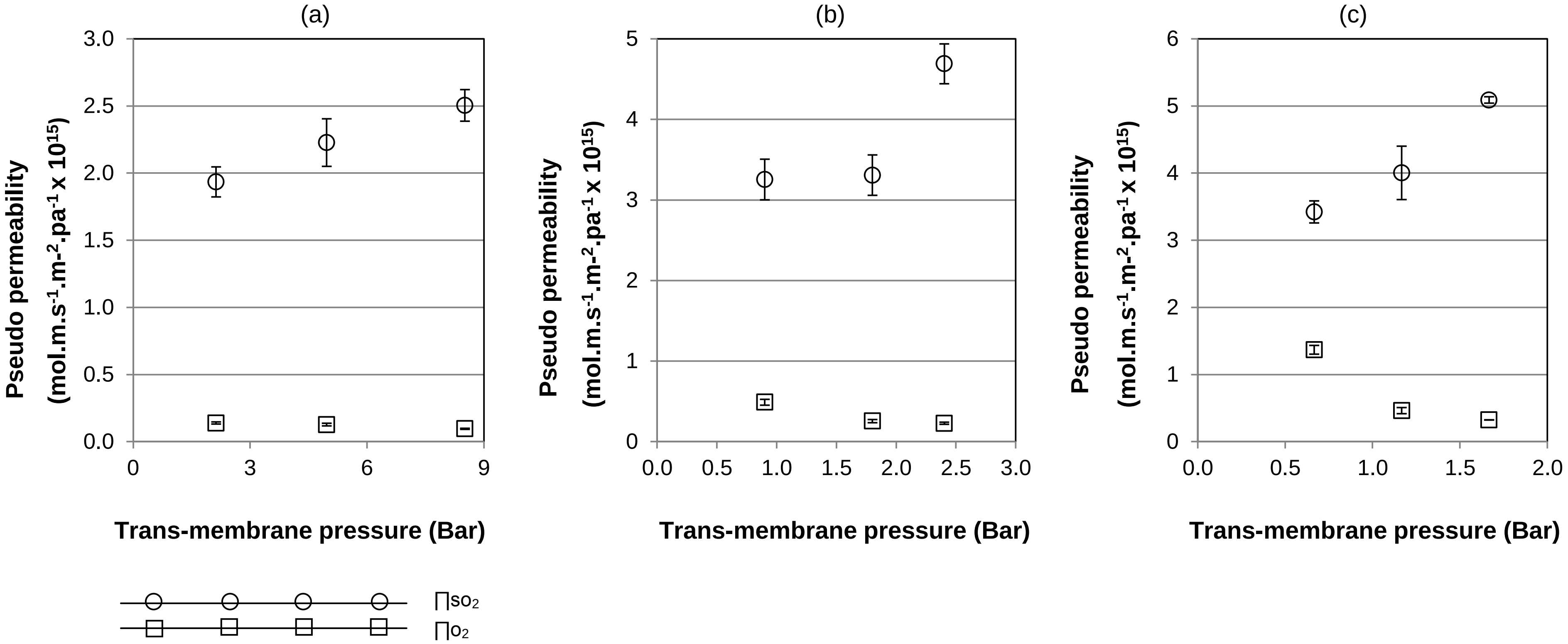


Figure 4.23 Effect of total trans-membrane pressure on SO_2 and O_2 pseudo permeability in Udel Polysulfone at 25°C with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 (c) 75 wt % feed SO_2

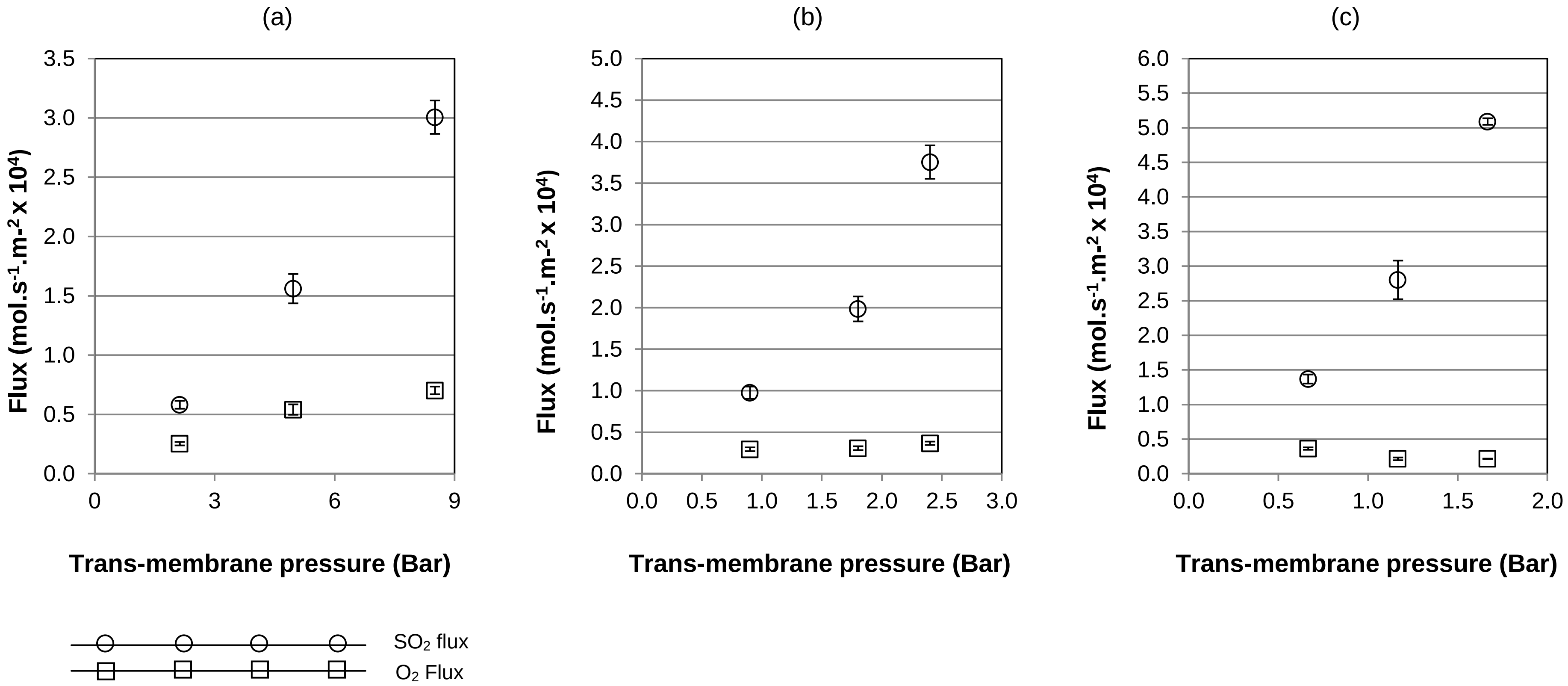


Figure 4.24 Effect of total trans-membrane pressure on SO_2 and O_2 molar flux in Udel Polysulfone at 25°C with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 (c) 75 wt % feed SO_2

With reference to Figure 4.22, a general increase in SO_2 composition in the permeate was observed with an increase in pressure. The behaviour presented is in agreement with the Dual mode sorption model that postulates that gas solubility increases in glassy polymers with an increase in pressure (Matteucci *et al*. 2006:40). The increased SO_2 solubility translated to increased SO_2 in the permeate. Despite the corresponding increase in O_2 partial pressure in the feed the low O_2 sorption potential was deemed insufficient to significantly increase O_2 in the permeate. O_2 generally has a much lower sorbing potential than SO_2 (The latter is discussed in Section 4.1.2)

Pfromm & Koros, (1993:6142) studied the sorption and transport behavior of SO_2 in Polysulfone. Findings from their study unearthed that the SO_2 sorption capacity in Udel Polysulfone was extremely high in comparison with that of N_2 (a permanent gas similar to O_2) with a vapor pressure of 7460.31 bar at 25°C and thus low condensability (Poling *et al*. 2008:2-59). SO_2 sorption parameters surpassed those of N_2 by up to two orders of magnitude. SO_2 with a low vapour pressure of 4 bar at 25°C has a high condensability and thus the sorption potential in glassy Udel Polysulfone is expected to be also high, whilst the low O_2 condensability evidenced by its high vapour pressure of 1817.53 bar at 25°C implied a low O_2 sorbing potential (The latter is also discussed in Section 4.1.2) (Poling *et al*. 2008:2-59; Poling *et al*. 2008:2-60). A net increase in SO_2 in the permeate thus resulted.

Figure 4.24 presents an increase in SO_2 flux with increasing trans-membrane pressure in all feed compositions attributed to the increase in driving force for permeability. O_2 flux however increased evidently with total trans-membrane pressure in Figure 4.24 (a) and then sluggishly in (b) and (c).

4.3.3 COMPARISON OF THE SO_2/O_2 SEPARATION POTENTIAL AND THE GAS FLUX THROUGH NAFION 117 AND UDEL POLYSULFONE

Figure 4.25 (a), (b), (c), (d) and (e) present graphs of permeate composition against feed composition for both Nafion 117 and Udel Polysulfone. The conditions considered were temperatures of 15°C to 55°C and a SO_2 trans-membrane partial pressure of $\Delta p_{SO2} = 1.1$ bar ± 0.2. The graphs have been plotted and extrapolated to the zero axis. The graphs are analogous to vapour liquid equilibrium graphs employed in distillation and can be used to estimate the number of separation stages required for a given membrane separation. It is from these graphs that a conclusion was made on which of the two membranes had an upper hand on SO_2/O_2 separation capability. Figures 4.26 (a), (b) and (c) present a comparison of the effect of temperature on SO_2/O_2 real selectivity in both Udel Polysulfone and Nafion 117. Figures 4.27 (a), (b) and (c) present graphs of permeate composition against feed composition for both Nafion 117 and Udel Polysulfone at diverse SO_2 feed partial pressures and constant temperature of 25°C. Figures 4.28 (a), (b) and (c) present a comparison of SO_2/O_2 real selectivity in Udel Polysulfone and Nafion 117 at diverse SO_2 feed partial pressures at 25°C. Figures 4.29 (a), (b) and (c) present a comparison of SO_2 and O_2 molar flux in Udel Polysulfone and Nafion 117 at varying temperatures and at a Δp_{SO2} of

1 bar ± 0.2. Figures 4.30 (a), (b) and (c) present a comparison of SO_2 and O_2 molar fluxes in Udel Polysulfone and Nafion 117 at varying total trans-membrane pressures and at 25°C.

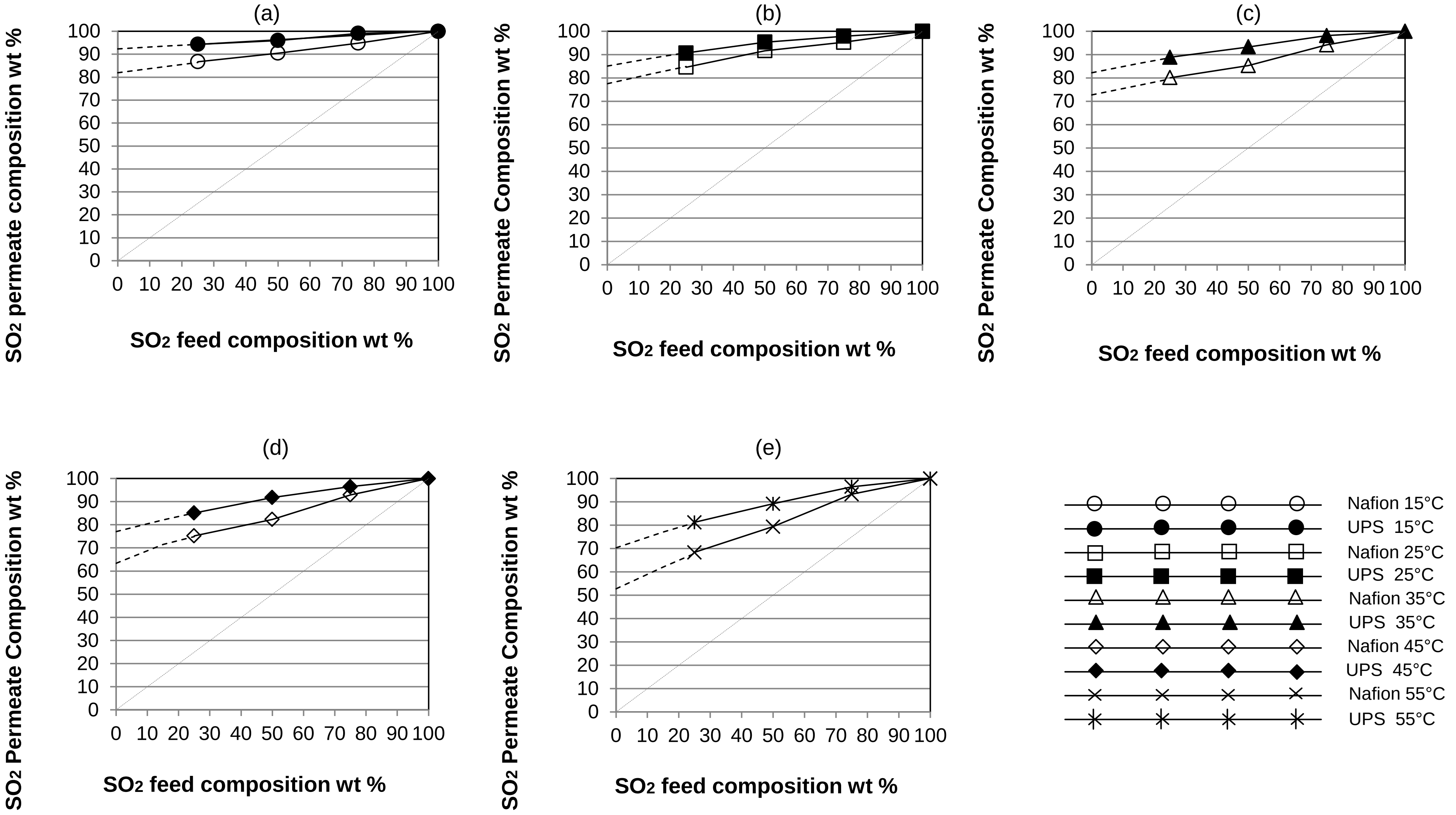


Figure 4.25 SO_2/O_2 separation potential of Nafion 117 and Udel Polysulfone at Δp_{SO2} 1.1 bar ± 0.2 and 5 different temperatures

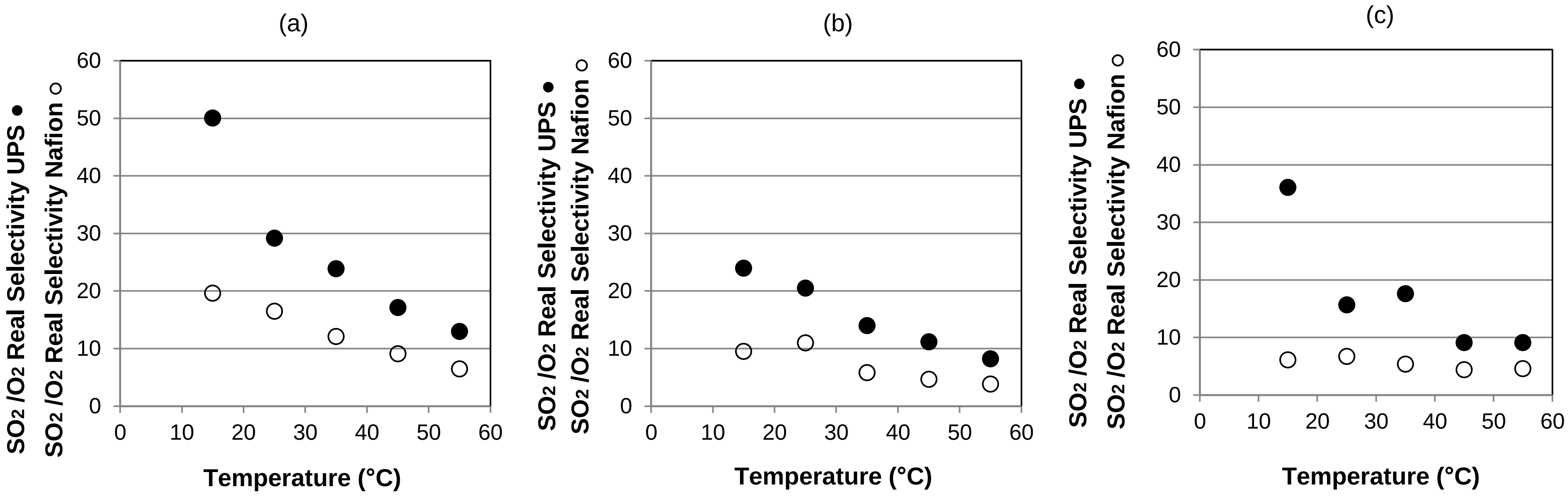


Figure 4.26 SO_2/O_2 selectivity in Udel Polysulfone and Nafion 117 at Δp_{SO_2} 1 bar ± 0.2 and 5 different temperatures with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 (c) 75 wt % feed SO_2

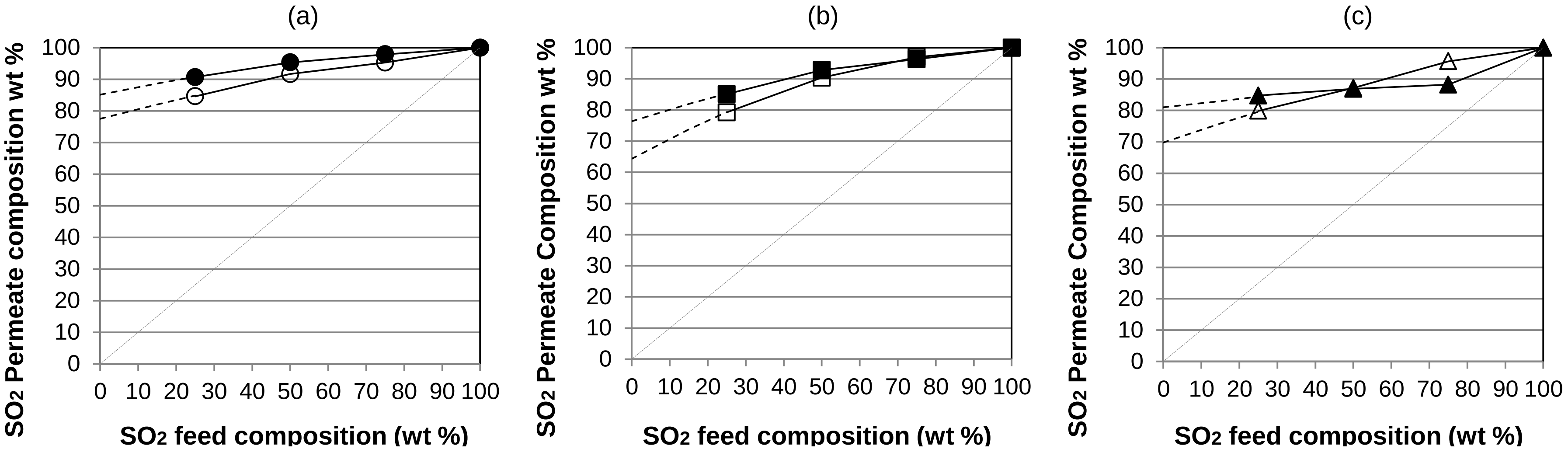
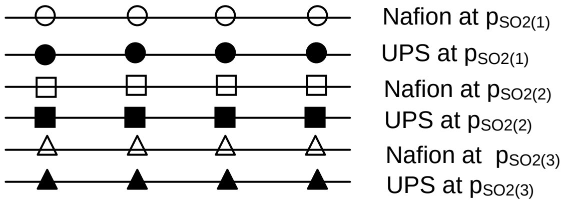


Figure 4.27 SO_2/O_2 separation potential of Nafion 117 and Udel Polysulfone at 25°C and at SO_2 feed partial pressures of $p_{SO2(1)}$, $p_{SO2(2)}$ and $p_{SO2(3)}$

Table 4.6 SO_2 partial pressure points

	Nafion 117			Udel Polysulfone		
Pressure	25% wt SO_2	50% wt SO_2	75% wt SO_2	25% wt SO_2	50% wt SO_2	75% wt SO_2
$p_{SO2(1)}$	2.4 bar	1.8 bar	2.0 bar	2.2 bar	1.6 bar	1.8 bar
$p_{SO2(2)}$	1.4 bar	1.2 bar	1.5 bar	1.8 bar	1.3 bar	1.5 bar
$P_{SO2(3)}$	1.3 bar	1.0 bar	1.1 bar	1.3 bar	1.0 bar	1.1 bar



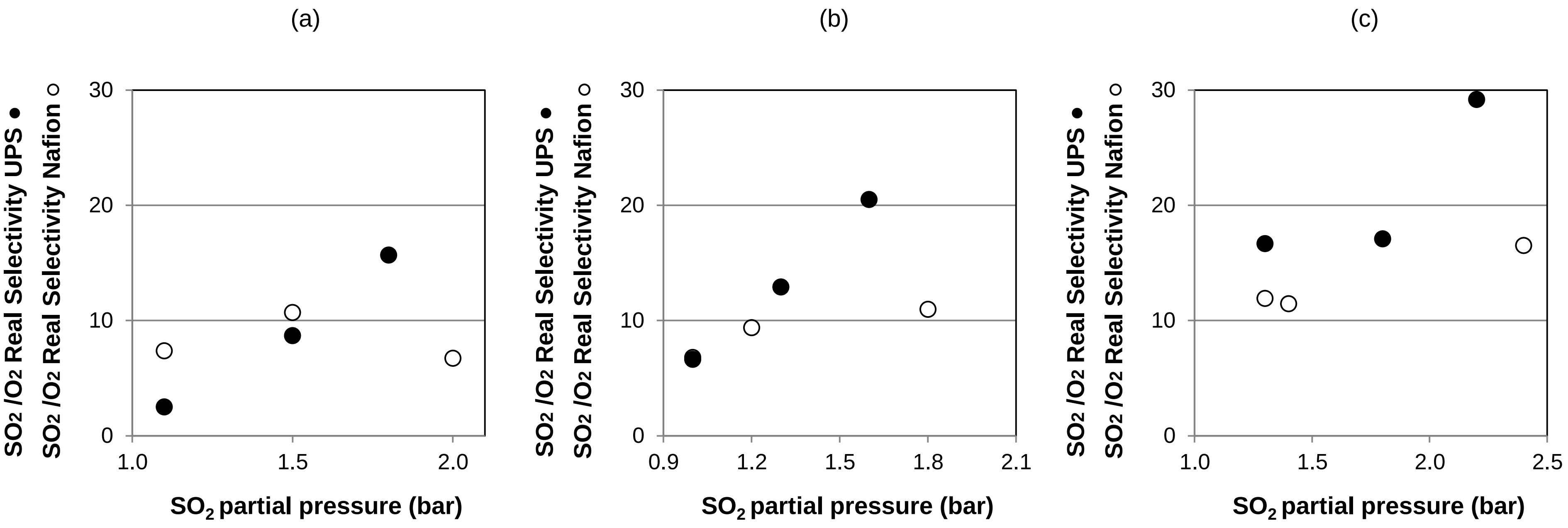


Figure 4.28 Comparison of SO_2/O_2 selectivity in Udel Polysulfone and Nafion 117 at diverse SO_2 feed partial pressures at 25°C with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 (c) 75 wt % feed SO_2

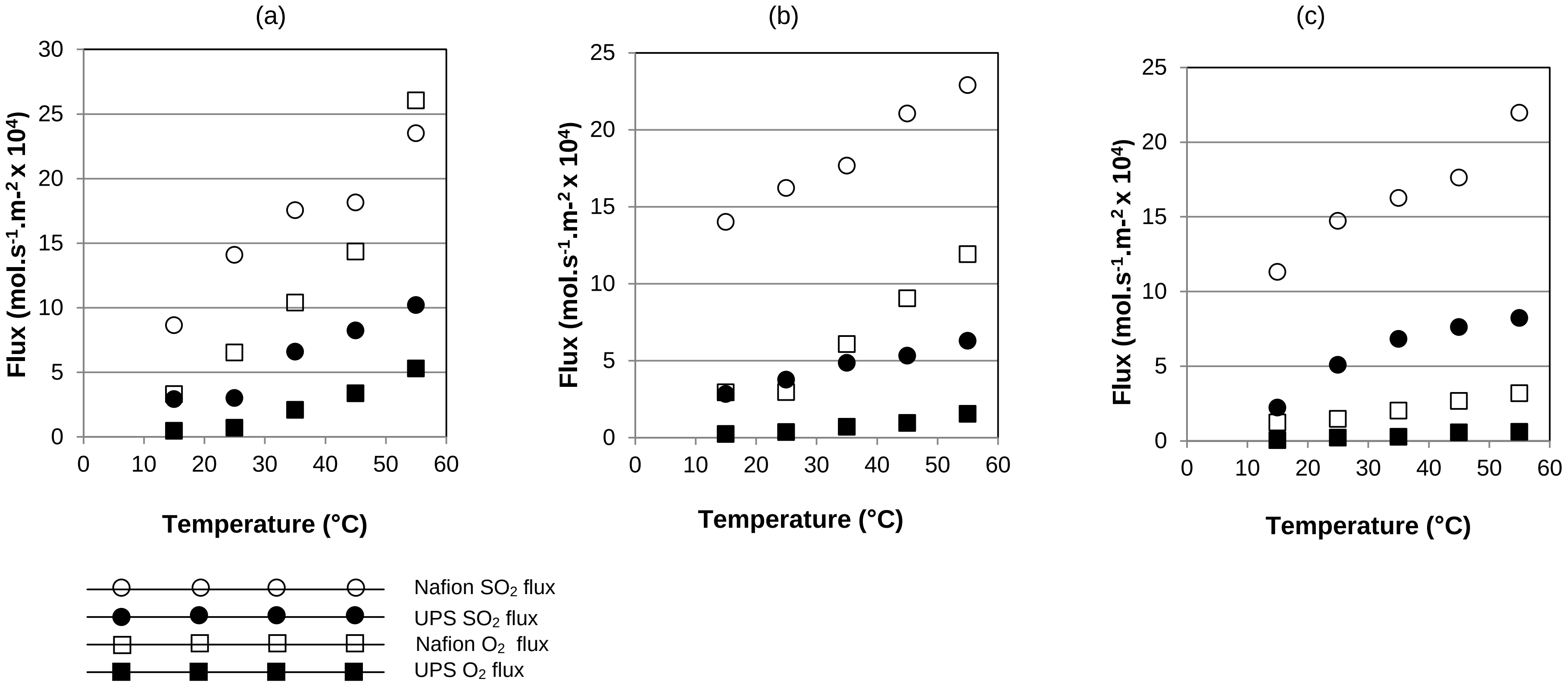


Figure 4.29 Comparison of SO_2 and O_2 molar flux in Udel Polysulfone and Nafion 117 at varying temperatures and at Δp_{SO2} 1 bar ± 0.2 with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 (c) 75 wt % feed SO_2

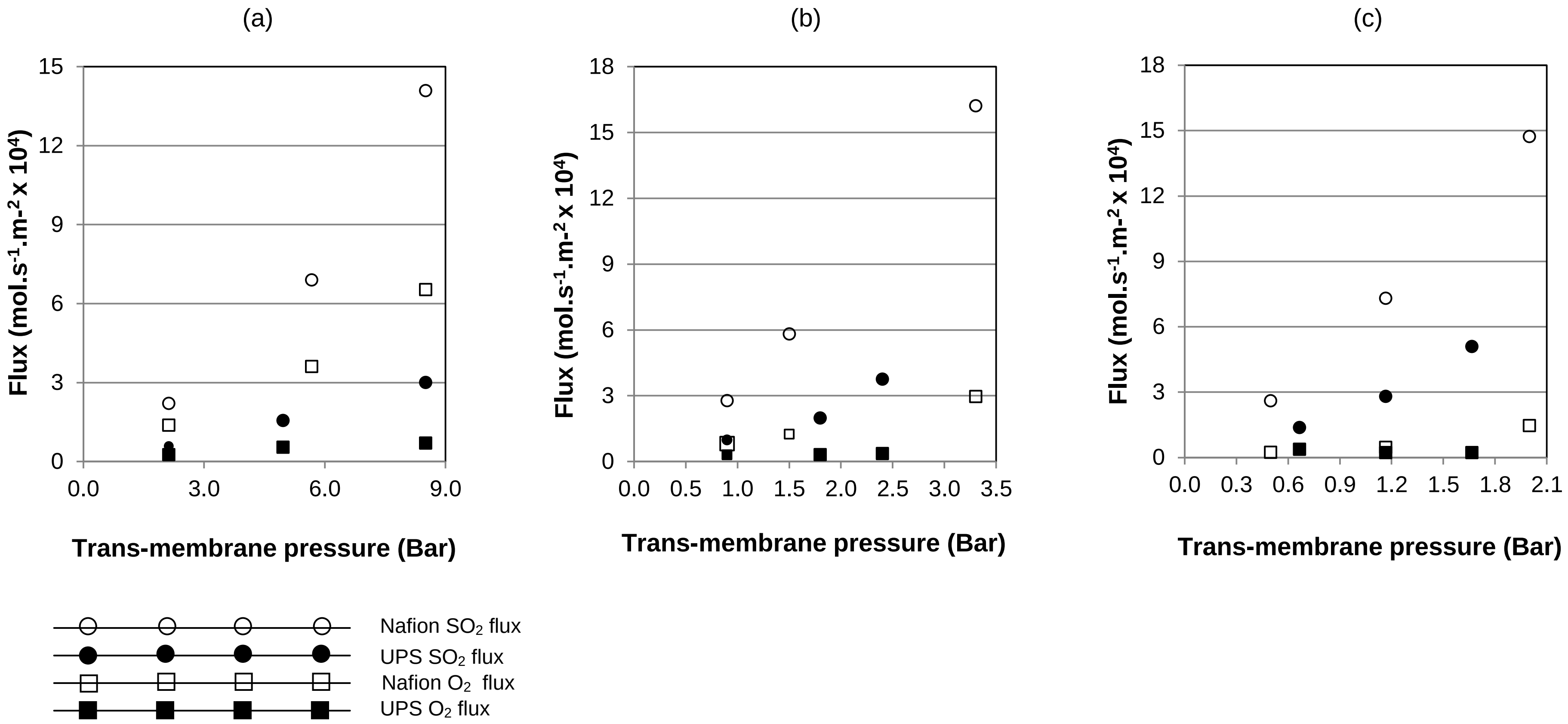


Figure 4.30 Comparison of SO_2 and O_2 molar flux in Udel Polysulfone and Nafion 117 at varying total trans-membrane pressures and 25°C with (a) 25 wt % feed SO_2, (b) 50 wt % feed SO_2 (c) 75 wt % feed SO_2

From Figures 4.25 (a), (b), (c), (d) and (e), it is clearly evident that Udel Polysulfone presented a much superior SO_2/O_2 separation capability at diverse temperatures at a constant trans-membrane pressure of 1.1 bar ± 0.2. Use of Nafion 117 instead of Udel Polysulfone to achieve a set separation would require more separation stages, as such translating to higher energy requirements for the process. Separation at low temperatures also would reduce the SO_2/O_2 separation stages. A similar conclusion was drawn from Figures 4.26 (a), (b) and (c) that Udel Polysulfone would separate SO_2 much more effectively than Nafion 117 within the temperature range considered. Figures 4.27 (a), (b) and (c) in a similar manner as Figures 4.25 (a), (b) and (c) present Udel Polysulfone as a membrane with a better separating potential than Nafion 117 at 25°C and diverse SO_2 feed partial pressures. The SO_2/O_2 selectivities in Udel Polysulfone at the different SO_2 feed partial pressures at 25°C also proved to surpass those presented in Nafion 117. The latter observation is shown in Figure 4.28.

The SO_2 flux values based on 1 µm thick hypothetical membranes given in Figures 4.29 (a), (b) and (c) were generally about a magnitude greater in Nafion 117 than in Udel Polysulfone. The higher fluxes observed in Nafion117 would come with the disadvantage of simultaneous increased O_2 flux. No wonder why the separation potential offered by Nafion 117 was inferior. Figures 4.30 (a), (b) and (c) also show Nafion to exhibit both higher SO_2 and O_2 fluxes with increased trans-membrane pressure.

4.4 CONCLUSION

Brunetti *et al*. (2011:286) proposed 8 inherent membrane characteristicts that would allow use of a membrane as a gas separation membrane.

1) High permeability
2) High selectivity
3) Thermal stability
4) Chemical stability
5) Plasticisation resistance
6) Aging resistance
7) Cost effectiveness
8) Ability to be manufactured into membrane modules

Based on the latter presented criteria, and the binary permeation results a comparison between Nafion 117 and Udel Polysulfone was made and presented in Table 4.7 so as to determine the candidate membrane with superior overall performance for the present application. The comparison was hinged on the binary gas experiments, where high permeability refers to the high SO_2 pseudo permeability and high selectivity refers to high SO_2/O_2 real selectivity. Thermal stability refers to stability within the predicted process temperature range (< 60°C) and chemical stability refers to the resistance to attack by sulphurous acid environments. Six of the criteria characteristics of the membranes were used for the comparison.

Table 4.7 Summary of overall membrane performance

Property	Udel Polysulfone	Nafion 117
High permeability	Good (1)	Excellent(1)
High selectivity	Excellent(1)	Good(1)
Thermal stability	Excellent(2)	Excellent(3)
Chemical stability	Excellent(4)	Excellent(5)
Plasticisation resistance	Fair(1)	Good(1)
Ability to be made into modules	Excellent(6)	Unknown

(1) Experimental results from present study (2) Solvay, (2011:24), (3) Dupont, (2009), (4) Solvay, (2011:33), (5) Orme & Stewart, (2009:512), (6) Wang *et al*. (2002:250)

The membranes seemed to stage competition against each other for superiority, the major shortfall of Udel Polysulfone being the resistance to plasticisation and the shortfall of Nafion

117 being the ability to form thin films in module form. Figure 4.4 of Section 4.2.1 presents the pressure dependence of the SO_2 permeability in Udel Polysulfone which takes the form of sceanarios where plasticisation is present as is also affirmed in Figure 2.4 (case 2) of Section 2.3. The much weaker pressure dependence of SO_2 permeability in Nafion 117 given in Figure 4.9 of Section 4.2.2 signified better resistance to plasticisation within the experimental range. Ismail & Lorna, (2002:37) presented a study that aimed to curb Udel Polysulfone plasticisation through heat treatment of the membrane. The latter technique could be used to increase the service life and efficiency of Udel Polysulfone. Ultra-thin films based on Nafion are unknown of at present, however, Udel polysulfone has been spun into ultra thin films less than 0.1 µm (Wang *et al*. 2002:250). As such Nafion 117 was disqualified from being a candidate for the present application. The superb SO_2/O_2 selectivity and superior resistance to SO_2 plasticisation of Nafion 117 evidenced by the weak pressure dependence of SO_2 permeability (*See Figure 4.9 of Section 4.2.2*) could prompt research on the synthesis of ultra-thin Nafion based membranes for SO_2/O_2 gas separation.

4.6 REFERENCES

[1] BAE,Y.S. & LEE, C.H. 2005. Sorption Kinetics of Eight Gases on a Carbon Molecular Sieve at Elavated Pressure. *Carbon* :95-107.

[2] BAKER, R.W. 2002. Future directions of membrane gas separation technology. *Industrial & Engineering Chemistry Research*, 41:1393-1411.

[3] BAKER, R.W. 2008. Vapour and Gas Separation by Membranes. (*In* Norman, N.L., Anthony, G.F., Wiston, W.S. & Matsuura, T., *eds.* Advanced Membrane Technology And Applications. New Jersey: John Wiley & Sons. p.559-580.)

[4] BIOGENERAL. 2012. Teflon AF Tubing and Membrane. http://www.biogeneral.com/teflon.html Date of access: 28 May 2012.

[5] BRECK, D.W. 1974. Zeolite Molecular Sieves: Structure, Chemistry and Use. New York: John Wiley & Sons. 771p

[6] BRUNETTI, A., BARBIERRI, G. & DRIOLI E. 2011. New metrics in Membrane gas separation. (*In* Drioli, E. & Barbieri, G., *eds.* Membrane engineering for the treatment of gases: Volume 2: Gas separation problems combined with membrane reactors. Cambridge: Royal Society of Chemistry. p.279-301.)

[7] CATALANO, J., MYEZWA, T., DE ANGELIS, M.G., BASCHETTI, M.G. & SARTI G.C. 2012. The Effect of Relative Humidity on the Gas Permeability and Swelling in PFSI membranes. *International Journal of Hydrogen Energy*: 6308-6316

[8] DHINGRA, S.S. 1997. Mixed Gas Transport Study through Polymeric Membranes: A Novel Technique. Blacksburg, Virginia:V.P.I.S.U. (Dissertation – Phd) 21p.

[9] DRODTEN, P. & SCHEDLITZKI, D. 2011. Carbon Dioxide. (*In* Schutze, M., Isecke, B. & Bender, R. *eds.* Corrosion Protection Against Carbon Dioxide. Weinheim: Wiley VCH. p.30-217.)

[10] DUPONT. 2009. Dupont Fuel Cells, Dupont Nafion PFSA Membranes. http://www2.dupont.com/FuelCells/en_US/assets/downloads/dfc101.pdf - Date of access: 21 May 2012.

[11] FRITZSCHE, A.K. & KURZ J.E. 1990. The Separation of Gases by Membranes. (*In* Porter, M.C., *ed.* Handbook of Industrial Membrane Technology. New Jersey: Noyes publications. p.559-593.)

[12] ISMAIL, A.F. & LORNA, W. 2002. Suppression of Plasticisation in Polysulfone Membranes for Gas Separations by Heat-Treatment technique. *Separation and Purification Technology*: 37-46, May.

[13] JAVAID, A. 2005. Membranes for solubility based gas separation applications. *Chemical Engineering Journal*, 112:219-226, 12 Jul.

[14] KOEV, I.L. (ikoev@biogeneral.com) 2 Nov. 2011. Data Sheet – Teflon AF 2400. Email to: Hlabano-Moyo, B.M. (22656227@nwu.ac.za).

[15] KOROS, W.J. 2004**.** Next Generation Membrane Materials & Structures for Energy-Efficient Gas Separations. http://www.aps.anl.gov/Science/Future/Workshops/Membrane_Science/Summaries/Koros.htm -Date of access: 20 June 2012.

[16] KOROS, W.J & CHERN, R.T. 1987. Separation of Gaseous Mixtures Using Polymer membranes. (*In* Rousseau, R.W., *ed*. Handbook of Separation Process Technology. New York: Wiley. p862-896.)

[17] MASSEY, L.K. 2003. Permeability Properties of Plastics and Polymers. New York: Plastics Design Library. 585p.

[18] MATTEUCCI, S., YAMPOLSKII, Y., FREEMAN, B.D & PINNAU, I. 2006. Transport of Gases and Vapors in Glassy and Rubbery Polymers. (*In* Yampolskii, Y., Pinnau, I. & Freeman, B. *eds.* Material Science of Membranes for Gas and Vapor Separation. Chichester: John Wiley & Sons. p.1-47.)

[19] MEYER, G.R. & THODOS, G. 1962. Viscosity and Thermal Conductivity of Sulphur Dioxide in the Gaseous and Liquid States. *Journal of Chemical and Engineering Data*, 7(4):532-536 Oct.

[20] NUNES, S.P. & PIENEMANN, K.-V. 2006. Part 1 Membrane Materials and Membrane Preparation. (*In* Nunes, S.P. & Pienemann, K.-V. *eds.* Membrane Technology in the Chemical Industry. Weinheim: Wiley VCH. p.3-92.)

[21] ORME, C.J., & STEWART, F.F. 2009. Pervaporation of Water from Aqueous Sulphuric Acid at Elevated Temperatures using Nafion Membranes. *Journal of Membrane Science*: 507-513.

[22] PARK, H.B. & LEE W.M. 2008. Polymeric Membrane Materials and Potential Use in Gas Separation. (*In* Norman, N.L., Anthony, G.F., Wiston, W.S. & Matsuura, T., *eds.* Advanced Membrane Technology And Applications. New Jersey: John Wiley & Sons. p.633-669.)

[23] PFROMM, P.H. & KOROS, W.J. 1993. Sorption and Transport of Sulphur Dioxide in Polysulfone. *Macromolecules*, 26:6141-6142.

[24] PHAIR, J.W. 2006. Materials for Separation Membranes in Hydrogen and Oxygen Production and Future Power Generation. *Science and Technology of Advanced Materials 7*: 702-805, Dec.

[25] POLING, B.E., THOMSON, G.H., FRIEND D.G., ROWLEY R.L. & WILDING, V.W. 2008. Physical and Chemical Data. (*In* Green D.W. & Perry R.H *eds.* Perry's Chemical Engineer's Handbook. New York: McGraw-Hill. p. 2-1 - 2-517.)

[26] SCHOLES, C.A., STEVENS, G.W. & KENTISH, S.E. 2012. Membrane Gas Separation applications in Natural Gas Processing. *Fuel*, 96:15-28, 18 Jan.

[27] SHIEH, J. & CHUNG, S.T. 1999. Gas Permeability, Diffusivity, and Solubility of Poly(4-Vinylpyridine Film). *Journal of Polymer Science: Part B: Polymer Physics*, 2851-2861: Jun.

[28] SIRCAR, S., RAO, M.B. & THAERON, C.M.A. 1999 Selective Surface Flow Membranes for Gas Separation. *Separation Science and Technology* :2081-2093.

[29] SODAYE, H.S., PUJARI, P.K., GOSWAMI. A., MANOHAR, S.B. 1997. Measurement of Free-Volume Hole Size Distribution in Nafion 117 Using Positron Annihilation Spectroscopy. *Journal of Polymer Science*: *Part B: Polymer Physics,*36: 983-989, 25 Sept.

[30] SOLVAY. 2006. Design and Processing Guide Halar ECTFE. http://www.solvaysolexis.asia/static/wma/pdf/9/2/1/9/BR_Halar.pdf Date of access: 28 Dec 2011.

[31] SOLVAY. 2008. Design and Processing Guide Hyflon MFA. http://www.solvaysolexis.asia/static/wma/pdf/1/6/4/7/1/Y42E002_Hyflon_MFA_Design_Processing_Guide_2009.pdf _Date of access: 28 Dec 2011.

[32] SOLVAY. 2011. Design Guide Udel Polysulfone. http://www.solvayplastics.com/sites/solvayplastics/EN/Solvay%20Plastics%20Literature/DPG_Udel_Design_Guide_EN.pdf Date of access: 28 May 2012.

[33] SOLVAY. 2012a. Gas Separation Membranes. http://www.solvayplastics.com/sites/solvayplastics/EN/specialty_polymers/Markets/Membranes/Pages/gas-separation.aspx Date of access : 11 Jan 2012.

[34] SOLVAY. 2012b. Design and Processing Guide Hyflon PFA. http://www.solvayplastics.com/sites/solvayplastics/EN/Solvay%20Plastics%20Literature/DPG_Hyflon_PFA_EN.pdf Date of access: 28 May 2012.

[35] STERN, S.A. & FRIED, J.R. 2007. Permeability of Polymers to Gases and Vapours. (*In* Mark. J.E., *ed*. Physical Properties of Polymers Handbook. New York: Springer. p.1033-1045.)

[36] STIEL, L.I., & THODOS, G. 1962. Lennard Jones Force Constants Predicted from Critical properties. *Journal of Chemical and Engineering Data*, 7(2): 234:236 Apr.

[37] VAN DER DONK, G. 2008. Inorganic Microporous Membranes for Gas Separation in Fossil Fuel Power Plants. Bochum: Forschungszentrum Jülich GmbH, Zentralbibliothek. 120p

[38] VICTOR, A., KUSUMA BENNY, D., FREEMAN. & MIGUEL, J., HAIQING L., SUMOD, K & DOUGLASS, S.K. 2008. Structure/Property Characteristics of Polar Rubbery Membranes for Carbon Dioxide Removal. (*In* Norman, N.L., Anthony, G.F., Wiston, W.S. & Matsuura, T., *eds.* Advanced Membrane Technology And Applications. New Jersey: John Wiley & Sons. p.929-950.)

[39] WANG, D., TEO, W.K. & LI, K. 2002. Preparation and characterisation of high-flux polysulfone hollow fibre gas separation membranes . *Journal of Membrane Science*, 1:333-353, 30 Jan.

[40] WESTERN ANALYTICAL. Tubing Reference Data. http://www.westernanalytical.com/pdf/Tube%20Ref%20Data.pdf Date of access: 28 May 2012.

[41] ZAVALETA, R. & McCANDLESS, F.P. 1976. Selective permeation through modified polyvinylidene fluoride membranes. *Journal of Membrane Science*, 1:333-353, 29 Mar.