

CHAPTER 2 : LITERATURE OVERVIEW

OVERVIEW

Chapter 2 constitutes of 5 main Sections namely, Application of membrane gas separation (Section 2.1), Principles of gas separation through membranes (Section 2.2), Critical parameters affecting gas transport in polymeric films (Section 2.3), State of the art review of SO₂ gas separation through membranes (Section 2.4) and the General review of SO₂ separation through membranes (Section 2.5). Section 2.1 gives the milestones achieved in the membrane gas separation timeline and the respective commercial applications of the technology. Section 2.2 details the underlying theories that drive membrane technology. Section 2.3 presents the effect of main process parameters that influence membrane gas separation performance. Section 2.4 gives a timeline review of the milestones that have been achieved in the transport and separation of SO₂ from gas mixtures through membranes. Section 2.5 then unearths the missing link that needs to be addressed in the field of SO₂/O₂ gas separation.

2.1 APPLICATION OF MEMBRANE GAS SEPARATION

The technology entails gas transport through a polymeric barrier that preferentially favours the transport of particular components whilst rejecting other components (Pandey & Chauhan, 2001:853). The differing transport behaviours are attributed to differing gas molecule – polymer molecule interactions (Pandey & Chauhan, 2001:860). A timeline is presented from the birth of the technology, the development of theories, through to the inception of commercial activity. The main aim being to fully appreciate the technology from its origins and probably have an imaginative view of what could be expected from the technology in the future. To have a broader perspective of the technology, current commercial applications are presented.

2.1.1 HISTORY OF MEMBRANE SEPARATION PROCESSES

J.K. Mitchell of Philadelphia pioneered the first membrane gas separations in 1831 (Paul & Yampol'skii, 1994:3). He noted that inflated balloons made of natural rubber and placed in gas atmospheres of diverse compositions blew up at different velocities depending on the type of the inflation gas (Paul & Yampol'skii, 1994:4). Of the examined gases, Mitchell noted that carbon dioxide was absorbed by rubber film to a larger extent in comparison to other tested gases (Paul & Yampol'skii, 1994:4). He was then led to infer that rubber expanded in volume and hence porosity was induced in the solid sample which provided a way of penetration of CO₂ molecules (Paul & Yampol'skii, 1994:4).

Round about the same time, Fick, a physiologist performed gas transport studies on Nitrocellulose membranes and these studies gave birth to what is commonly known as “Fick's first law” (Paul & Yampol'skii, 1994:4).

Thomas Graham of the University College London in 1866 then published a paper that presented “Graham's Law of effusion” (Paul & Yampol'skii, 1994:4). He repeated Mitchell's experiments and became the first to conduct quantitative measurements of the rate of gas permeation (Paul & Yampol'skii, 1994:4). Through Mitchell's experiments, he established several relative permeation rates across a film for a number of gases (Paul & Yampol'skii, 1994:4). No relation was found between experimental values and known diffusion coefficients in gases (Paul & Yampol'skii, 1994:4). The latter then led to the proposal of the solution-diffusion mechanism (Paul & Yampol'skii, 1994:4).

Lots of the early experimental work in gas permeation could be wholly attributed to Graham (Paul & Yampol'skii, 1994:4). He performed the first membrane gas separation and obtained

oxygen enriched air (46.6% oxygen) (Paul & Yampol'skii, 1994:4). Graham proposed that pressurising a gas mixture to be separated would aid in increasing the gas flux across the separating film (Paul & Yampol'skii, 1994:4). He also observed that the film thickness affected only the gas flux and not the permeate composition (Paul & Yampol'skii, 1994:4). Graham noted the effect of temperature on gas permeation, an increase in temperature led to a decrease in penetrant solubility, but made the membrane more permeable (Dhingra, 1997:14). Graham synthesised the first composite membranes and also went on to describe his experiments on hydrogen permeation across platinum and palladium membranes and concluded they as well as rubber films behaved like non-porous septa (Paul & Yampol'skii, 1994:4).

With the progression of time, Aronstein and Sirks discovered that also water vapour permeated through polymeric films (Paul & Yampol'skii, 1994:5). Exner observed gas permeation across liquid soap films and showed that permeation rate of a penetrant through the soap film is directly proportional to the product of diffusivity and solubility of that penetrant in the film (Koros & Chern, 1987:863). The latter observations on the permeation rates of different gases showed that high solubility in conjunction with high diffusivity is the condition for high permeation fluxes (Paul & Yampol'skii, 1994:5). The latter claim was then quantitatively presented by von Wroblewski who then defined the permeability coefficient as the product of the volumetric flux and the ratio of film thickness to trans-film pressure (Paul & Yampol'skii, 1994:5). He also went on to present the permeability coefficient as a product of solubility and diffusivity (Paul & Yampol'skii, 1994:5).

All these studies presented prior, pertain to steady fluxes across a membrane film. It was only after about half a century that H.A. Daynes designed equipment that could be used both for transient and steady state transport across a membrane film (Paul & Yampol'skii, 1994:5). Daynes noted that gas diffusion through a rubbery film is determined by two more or less separate processes such that by measurement of permeability alone, a complete understanding of the gas transport would not be arrived at (Paul & Yampol'skii, 1994:5). Through the use of Fick's second law of diffusion for calculating the diffusion coefficient, Daynes presented a mathematical solution through the introduction of the "time lag" method which is still in use today in estimating the gas diffusion coefficient (Dhingra, 1997:16).

In the 1930s and 1940s, R.M. Barrer widely introduced Daynes methods to experimental practice to yield the Daynes-Barrer method (Paul & Yampol'skii, 1994:5). The unit Barrer for the permeability coefficient was given in recognition of his works (Paul & Yampol'skii, 1994:5).

Commercial gas separation through the use of polymeric membranes was then initiated in 1980, after the failure of the thick dense polymeric membranes to give effective permeation fluxes in the 1970's because of their thick matrices (Park & Lee, 2008:634).

Figure 2.1 presents a membrane technology timeline in the 20th century.

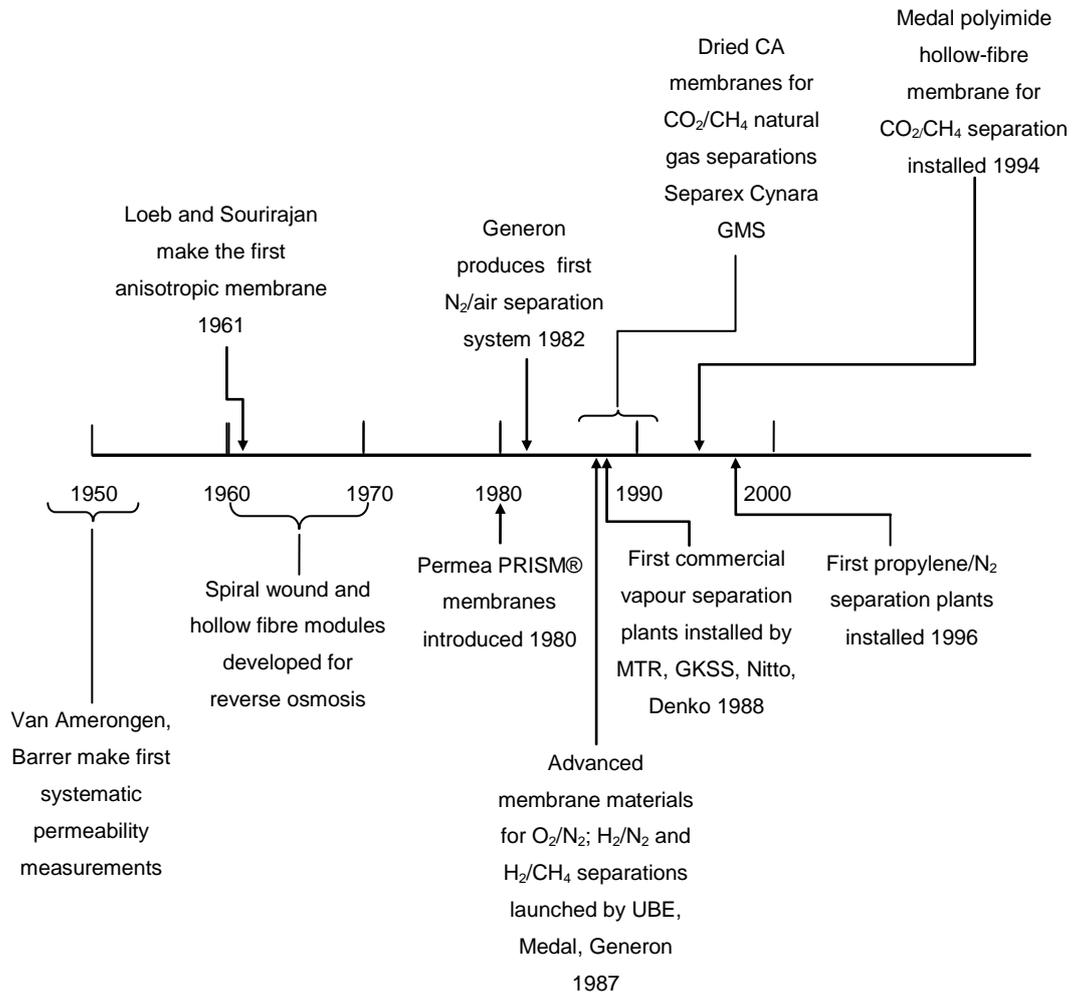


Figure 2.1 Membrane gas separation timeline (Adapted from Baker, (2002:1394))

Figure 2.1 highlights that commercial gas separation through the use of membranes is a relatively young technology, just above 30 years, as such diverse aspects of the technology are still to be fully appreciated.

2.1.2 COMMERCIAL APPLICATIONS OF MEMBRANE GAS SEPARATION

Gas separation through the use of dense polymeric membranes for gas separation have found diverse applications ranging from the food and packaging industry, medical fraternity, oil and gas industry, wastewater treatment, chemical process industry just to mention a few. Though young a technology it could be, it has found use in the latter industrial applications and thus there is no question of its capability to address the problem at hand on an industrial scale. The commercial applications are given in Table 2.1.

Table 2.1 Commercial applications of membrane gas separation

| Gas Separation | Commercial Application | Source |
|--|--|--|
| O ₂ /N ₂ | Enrichment of O ₂ for enhanced combustion, respiratory supplement for patients and aerobic treatment of waste water. Enrichment of N ₂ for blanketing flammable environments and preserving freshness of food | (US Dept of Energy, 2011; Innovative Gas Systems, 2012; Robeson, 1999:551) |
| Natural gas/CO ₂ /H ₂ S/H ₂ O | Natural gas purification | (Innovative Gas Systems, 2012; Robeson, 1999:551) |
| He/Air/Natural gas | Helium recovery from air and natural gas | (Innovative Gas Systems, 2012; Robeson, 1999:552) |
| H ₂ /Hydrocarbons | Hydrogen purification from steam and natural gas reforming | (Innovative Gas Systems, 2012), |

2.2 PRINCIPLES OF GAS SEPARATION THROUGH MEMBRANES

The equations governing the transport of gases in membranes are presented in conjunction with the expected behavior of diverse polymer - penetrant systems. The effect of critical process parameters on the gas transport behavior in polymers is also brought to light.

2.2.1 POLYMERIC MEMBRANES IN GAS SYSTEMS

Much focus in the present study is biased towards the use of dense polymeric films which constitute of rubbery and glassy polymers. Rubbery polymers exist above their glass transition temperature (T_g) at ambient conditions (Kholodovych & Welsh, 2007:612). Rubbery polymeric films generally offer higher gas permeabilities through them, whilst rendering low selectivity (Stern & Fried, 2007:1037). The latter may be attributed to the high flexibility of their polymer chains. Separation of gases in rubbery polymers is often hinged on differing gas solubilities in the polymer (Stern & Fried, 2007:1037), which can further be elaborated as differing intermolecular interactions between penetrant and polymer molecules. The rubbery films generally exhibit preferential permeability to larger molecules (Malykh *et al.* 2010:90). On the other hand, glassy polymers exist below their glass transition temperature (T_g) at ambient conditions (Kholodovych & Welsh, 2007:612). In contrast to rubbery films, glassy films generally present low gas permeabilities, while offering high gas selectivity (Stern & Fried, 2007:1037). Differing gas diffusivities in the polymer often dictate separation (Stern & Fried, 2007:1037). The latter implies that the smaller gas molecules dominate in permeability which is characteristic of low free volume glassy polymers (Malykh *et al.* 2010:90). High free volume glassy polymers however present a behavior similar to that of rubbery polymers with a few exceptions (Malykh *et al.* 2010:90).

2.2.2 FUNDAMENTALS OF GAS TRANSPORT IN NON-POROUS DENSE POLYMERIC FILMS

The solution-diffusion model fully describes gas transport through non-porous polymeric films (Park & Lee, 2008:635). The model can be summarised as is given in Equation 2.1. It is further elaborated on in the third paragraph of Section 2.2.2.

$$P = DS \quad (2.1)$$

Where P is the permeability coefficient, D is the gas diffusivity, and S is the gas solubility in the polymer. Gas transport in dense polymeric films is established by the chemical potential gradient of permeating species, which is the trans-film pressure (Malykh *et al.* 2010:90). Equation 2.2 gives a summary of the mechanism of gas transport in dense polymers, which entails transport of the gas through the boundary layer, absorption of a gas into a membrane

on the high pressure side, diffusion through the matrix, desorption on the low pressure side and finally diffusion through the downstream boundary layer (Stern & Fried, 2007:1037; Park & Lee, 2008:635).

$$\frac{V^i}{A} = \frac{P\Delta p}{l} \quad (2.2)$$

Where V^i is the volumetric flow rate, A is the cross-sectional area of the membrane, P is the permeability of the membrane, Δp is the trans-membrane pressure and l the membrane thickness. The permeability coefficient (P) also known as the permeability is a product of two crucial parameters, Diffusivity(D), a kinetic term and Solubility(S), a thermodynamic term (Matteucci *et al.* 2006:2). The permeability coefficient is a proportionality constant in Equation 2.1 that defines gas transport as an intrinsic property of a polymer/gas pair (Matteucci *et al.* 2006:1). Diffusivity merely is the movement of gas molecules through the polymer, whilst solubility is the quantity of dissolved gas molecules in the membrane material (Baker, 2008:635).

2.2.2.1 Diffusion modes in dense polymeric films

The modes of diffusion in a given polymer-penetrant system differ from one another depending on the relative mobility between the gas and the polymer chains as is outlined. Three typical cases in which the diffusion coefficient is independent of penetrant concentration are given.

- I. Fickian diffusion, which is characterised by penetrant motion that is sluggish in comparison to the motion of the polymer chains and is related to the square root of time (Dhingra, 1997:58). Supercritical gases present the Fickian form of diffusion in rubbery polymers (Dhingra, 1997:18).
- II. Non-Fickian diffusion, which is characterised by high diffusion rates that surpass polymer chain motion. The latter phenomenon is time dependant and leads to polymer swelling (Dhingra, 1997:58).
- III. Anomalous diffusion, which occurs in scenarios where the diffusion rate and polymeric chain motions are comparable. In case (iii), the polymer micro-structure

and microvoids affect the transport and sorption of penetrant across the polymer (Park & Lee, 2008:635).

In some cases however, the diffusion coefficient tends to be hinged on the penetrant concentration, and thus exhibits penetrant concentration dependent forms presented in Figure 2.2

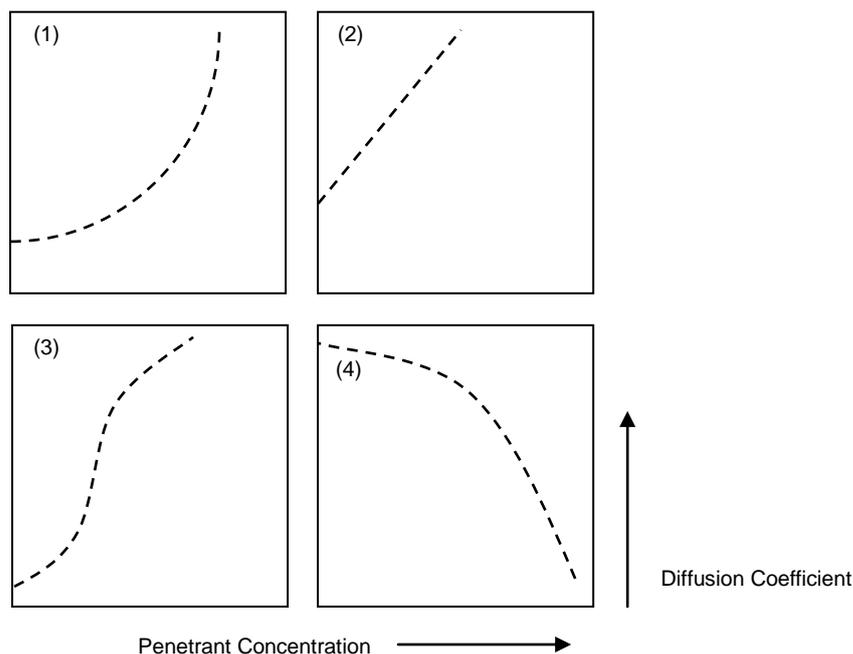


Figure 2.2 Concentration dependence of diffusion coefficient
(Adapted from Dhingra (1997 :47))

Case (1) represents the diffusion of plasticising penetrants such as the transport of organic vapours in hydrocarbon membranes, the diffusion coefficient increases exponentially as penetrant concentration is increased. The second case depicts a linear relationship which results at low plasticising penetrant concentrations. The third case with an inflexion is characteristic of diverse penetrant types in glassy polymers at low concentrations. Agglomeration of molecules tends to occur due to the presence of intermolecular forces such as hydrogen bonds (Koros & Chern 1987:888).. The overall diffusion of agglomerates through polymeric films tends to fall due to the increased size of penetrant (Koros & Chern 1987:888). The agglomerates in question tend to grow with increased penetrant concentration or pressure, thus resulting in the behaviour depicted by case (4), a decrease of the diffusion coefficient with increased concentration (Koros & Chern 1987:888).

2.2.2.2 Solubility modes in dense polymeric films

Just as different diffusion modes exist, diverse solubility or sorption modes also exist depending on the polymer type, whether glassy or rubbery. Focus will only be on five modes.

1. Henry's Law sorption, which is predominant in rubbery polymers and in low concentration gas sorption in glassy polymers is given by Equation 2.3 (Dhingra, 1997:18; Koros & Chern 1987:886)

$$C = Sp \quad (2.3)$$

Where C, is the concentration of dissolved gas in the polymer, p is the gas partial pressure of gas, S is the Henry's solubility constant for the specific polymer-gas pair (Fritzsche & Kurz, 1990:564).

2. Langmuir sorption, which is given by equation 2.4.

$$C = \frac{C^*bp}{1+bp} \quad (2.4)$$

3. Dual mode sorption model that is merely a hybrid of the Henry's law sorption and the Langmuir sorption, and is given by Equation 2.5. The sorption behaviour is characteristic of gas transport in glassy polymers at moderate pressures (20-30atm) (Koros & Chern 1987:886)

$$C = C_D + C_H = k_Dp + \frac{C'_Hbp}{1+bp} \quad (2.5)$$

Where, C is the overall concentration of sorbate in the polymer, C* is the saturation concentration of adsorbed sorbate in the polymer, C_D and C_H are the gas concentrations dissolved and adsorbed in the polymer respectively and p is gas pressure. K_D is the Henry's law constant, C'_H is the Langmuir capacity constant and b is the affinity constant (Park & Lee, 2008:640).

4. Flory-Huggins mode sorption which is characteristic of penetrants that are compatible with the rubbery polymer and thus enhance polymer swelling. Penetrants possessing hydrogen bonds and the complex polar penetrants which have a clustering tendency also exhibit the Flory-Huggins sorption behaviour in non-polar rubbery polymers (Koros & Chern 1987:886; Park & Lee, 2008:640).
5. Brunauer-Emmett-Teller sorption mode is a complex sorption form that is characteristic of vapours and highly sorbing gases in glassy polymers (Koros & Chern 1987:886)

A graphical view of the sorption modes is presented in Figure 2.3

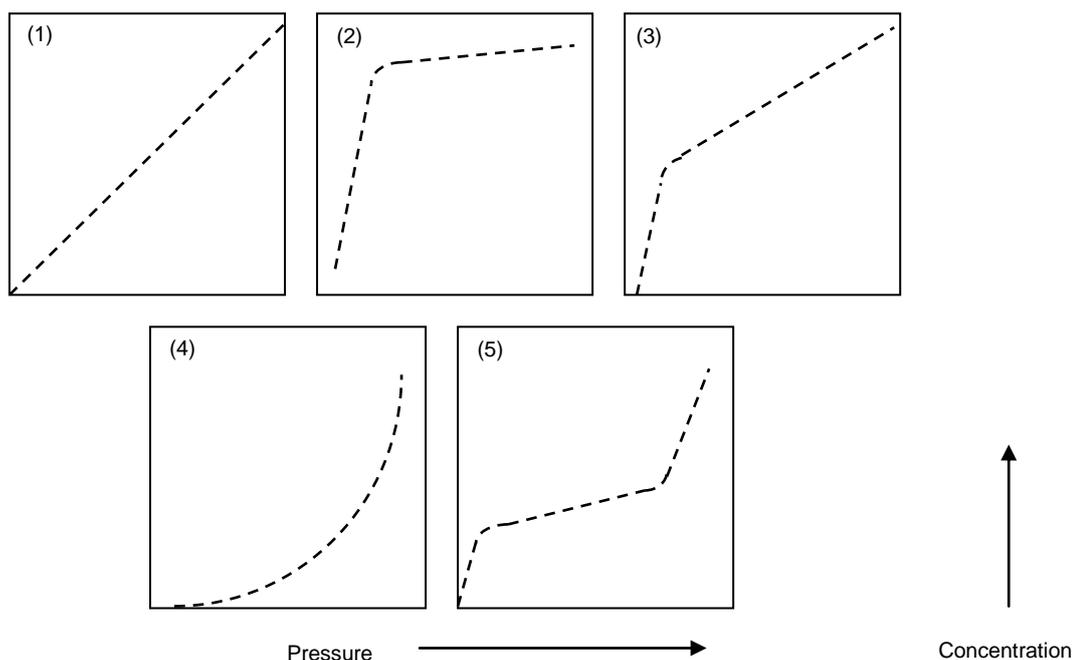


Figure 2.3 Sorption modes (Adapted from Park & Lee (2008:636))

2.2.2.3 Permeability and Selectivity

It is often highly desirable to employ a membrane that offers both high permeability or volumetric flux and high selectivity, but this is not always feasible. Either one or the other is high! A trade-off generally exists between permeability and selectivity. Polymers exhibiting high permeability have low selectivity and vice-versa (Matteucci *et al.* 2006:4). “*One cannot have the cake and eat it!*”

Permeability already has been defined as the product of diffusivity and solubility in Section 2.2.2. Selectivity can then be defined by the “ideal” separation factor which is a ratio of the permeabilities of the two penetrants to be separated or a product of the solubility selectivity and diffusivity or mobility selectivity. Given that there are two components, (1 and 2) to be separated their ideal separation factor can be presented as is given in Equation 2.6.

$$\alpha_{1/2} = \frac{P_1}{P_2} = \frac{D_1}{D_2} \cdot \frac{S_1}{S_2} \quad (2.6)$$

Where $\alpha_{1/2}$ is the ideal separation factor, P_1 and P_2 are the respective permeabilities of components 1 and 2. The diffusivity selectivity (D_1/D_2) and the solubility selectivity (S_1/S_2) are merely contributions to the total selectivity (Stern & Fried, 2007:1035). The ideal separation

factor is based on pure component permeability and can be used as an approximation of actual or real selectivity. However it is still critical to evaluate the actual selectivity experimentally (Dhingra, 1997:18).

2.3 CRITICAL PARAMETERS AFFECTING GAS TRANSPORT IN POLYMERIC FILMS

The main variables that govern gas transport in polymers are temperature, pressure and gas composition.

2.3.1 TEMPERATURE

At isobaric conditions, gas diffusion across a polymeric film increases with temperature as long as the polymer does not undergo degradation or crystallization. The relationship obeys Arrhenius behavior as is given in Equation 2.7 (Park & Lee, 2008:638; Stern & Fried, 2007:1036).

$$D = D_0 \exp\left[\frac{-E_D}{RT}\right] \quad (2.7)$$

Where, D is the diffusion coefficient, D_0 is a pre-exponential factor. E_D is the diffusion activation energy in $\text{kJ}\cdot\text{mol}^{-1}$, which is the energy required to overcome attractive forces between polymer chains through which the gas molecules traverse. E_D is dependent on polymer morphology and on the thermal properties of the polymer, R is the universal gas constant ($8.314 \text{ Jol}\cdot\text{mol}^{-1}\cdot\text{k}^{-1}$) and T is the absolute temperature in Kelvin (Park & Lee, 2008:638).

Solubility also depends on temperature, and is summarised by a Van't Hoff relationship given in Equation 2.8.

$$S = S_0 \exp\left[\frac{-\Delta H_s}{RT}\right] \quad (2.8)$$

Where S is the solubility, ΔH_s is the enthalpy of solution of the sorbate which in a like manner as E_D depends on the morphology of the polymer and on the polymer's thermal properties and S_0 is a pre-exponent factor (Park & Lee, 2008:638).

Permeability, the product of diffusivity and solubility as given in Equation 2.1 can then be presented thus, through the use of Equations 2.7 and 2.8.

$$P = D_0 \exp\left[\frac{-E_D}{RT}\right] S_0 \exp\left[\frac{-\Delta H_S}{RT}\right] \quad (2.9)$$

Equation 2.9 then simplifies to Equation 2.10 :

$$P = P_0 \exp\left[\frac{-E_P}{RT}\right] \quad (2.10)$$

Where P is the permeability coefficient, E_P is the permeation activation energy which is a summation of the diffusion activation energy (E_D) and the enthalpy of solution of sorbate (ΔH_S) and P_0 is a pre-exponential factor (Park & Lee, 2008:638). The latter discourse presents that permeability and temperature are related through an Arrhenius relationship.

2.3.2 PRESSURE

Koros & Chern, (1987:885) placed emphasis on the importance of pressure as a vital variable in gas transport and suggested that accurate modelling of membrane permeators is possible only with knowledge of the composition and pressure dependence of the gas transport at given isothermal conditions.

The permeability behaviour of gases as a function of pressure as presented by Koros & Chern, (1987:885) is given in Figure 2.4.

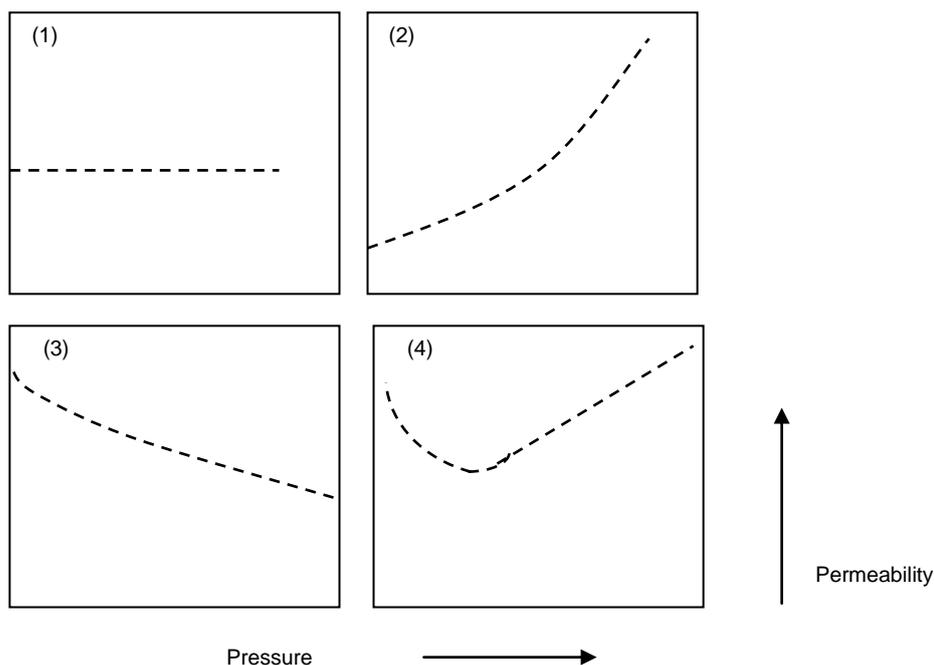


Figure 2.4 Pressure dependence of permeability (adapted from Koros & Chern, (1987:885))

The behaviour represented by (1) in Figure 2.4 is typical of scenarios where both the diffusivity and solubility coefficients are constants i.e. they are not dependent on pressure (Koros & Chern, 1987:885). The presented behavior occurs with supercritical gases (gases with very low critical temperatures) such as O_2 , N_2 , H_2 just to mention a few, as the concentration of supercritical gases in rubbery polymers remains within Henry's law limit even at high pressures (Stern & Fried, 2007:1036). Plasticising penetrants in polymers exhibit a behaviour depicted by (2) (Koros & Chern, 1987:885; Park & Lee, 2008:638). A highly soluble gas such as CO_2 would present a behaviour given by (3) in glassy polymers, which depicts a decrease in permeability with increased pressure (Park & Lee, 2008:639). The first three scenarios generally occur at much lower pressures as compared to scenario (4) which is typical of the high pressure transport of a plasticising penetrant traversing through a polymer type that is plasticisation resistant at low pressure such as the glassy polymer (Koros & Chern, 1987:885; Park & Lee, 2008:639). Considerable plasticisation of the glassy polymer occurs as pressure is increased significantly (Stern & Fried, 2007:1036).

2.4 STATE OF THE ART REVIEW OF SO₂ GAS SEPARATION THROUGH MEMBRANES

Several authors have investigated the transport behavior of SO₂ through polymeric materials. Diverse experimental conditions and membrane types have been used. However there still is a great deal of knowledge that is lacking in the field as such the need for ongoing research is due. Research work on SO₂ transport through membranes is therefore presented in Tables 2.2, 2.3 and 2.4 in an effort to identify the loose ends.

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Table 2.2 State of the art SO₂ gas transport in membranes

| Year | Conditions | Membrane | Components | Ideal Selectivity | SO ₂ Permeability/Flux | Source |
|------|---|--|--|--|--|-----------------------------------|
| 1974 | Pressure: 6.89 – 34.47 Bar Temperature: 14 - 75°C Gas Composition: 0 – 12 wt % SO ₂ , balance N ₂ Membrane Thickness: 25.4 μm Sulfolane Content in Membrane: 0 – 20 wt% | Sulfolane plasticised vinylidene fluoride film | SO ₂ & N ₂ | α_{SO_2/N_2} : 30 - 100 | Flux = 0.02 -1.86 scfd/ft ² | (Seibel & McCandless, 1974:76) |
| 1976 | Partial SO ₂ trans-membrane pressure: 0 – 2.76 Bar Trans-membrane pressure for all gases: 6.89 – 48.26 Bar Temperature: 0 - 55°C Gas Composition: Pure gases, Binary (5.6 % SO ₂ balance N ₂) (42% CO ₂ balance H ₂) Membrane thickness:25.4μm & 50.8 μm | Sulfone modified polyvinylidene fluoride | SO ₂ , N ₂ , CO ₂ , Ar, O ₂ , H ₂ , CH ₄ , CH ₃ CH ₃ , CH ₂ CH ₂ , C ₄ H ₆ | α_{SO_2/N_2} : 30 – 500 α_{CO_2/H_2} : 1.5 - 3 | Maximum SO ₂ permeability = 0.518 x 10 ⁻⁶ cm ³ (STP).cm/(cm ² .s.cmHg | (Zavaleta & McCandless, 1976:333) |
| 1980 | Pressure: 1 Bar upstream pressure Temperature: 24 – 26°C Gas Composition: Pure gases Membrane Thickness: Polyacrylate (0.72 – 267 μm) Membrane Thickness: Cellulose Triacetate (0.051 – 0.125 μm) | Polyacrylate & Cellulose Triacetate | SO ₂ , N ₂ & CO ₂ | α_{SO_2/CO_2} : 7.16 – 21.2 α_{SO_2/N_2} : 116 - 329 | Polyacrylate SO ₂ Permeability = 378 – 5160 cm ³ (STP).cm/(cm ² .s.cmHg x10 ¹⁰ , Cellulose Triacetate SO ₂ permeability = 364 - 786 cm ³ (STP).cm/(cm ² .s.cmHg x10 ¹¹ | (Kuehne & Friedlander, 1980a:616) |
| 1980 | Single permeation pressure: 1 Bar for N ₂ & CO ₂ , 0.132 – 1 Bar for SO ₂ . Binary permeation (SO ₂ /N ₂); 10 Bar upstream & 0.2 Bar downstream Temperature: 25 - 27°C Gas Composition: Pure SO ₂ , N ₂ & CO ₂ . Binary (1-10% SO ₂ in N ₂) Membrane thickness: 0.179 – 0.485 μm | Polyacrylate/ Cellulose Triacetate composites | SO ₂ , N ₂ & CO ₂ | α_{SO_2/CO_2} : 2.14 – 7.37 α_{SO_2/N_2} : 14.2 – 111 | Cellulose Triacetate/ Polyacrylate composites SO ₂ Permeability = 50.6 – 758 cm ³ (STP).cm/(cm ² .s.cmHg x10 ¹⁰ | (Kuehne & Friedlander, 1980b:609) |

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Table 2.3 State of the art SO₂ gas transport in membranes

| Year | Conditions | Membrane | Components | Ideal Selectivity | SO ₂ Permeability/Flux | Source |
|------|---|---|---|---|--|--|
| 1983 | Pressure: 0 – 2.5 Bar Temperature: 10 - 50°C Gas Composition: Pure gases Membrane thickness: 64 -170 μm | Polyvinyltrimethyl Silane | SO ₂ | - | SO ₂ permeability = 30 mole.cm ⁻¹ .s ⁻¹ .Pa ⁻¹ x 10 ⁻¹⁷ | (Yampol'skii <i>et al.</i> 1983:1832) |
| 1985 | Feed Pressure: 0 – 5 Bar Temperature: 17 -24°C Gas Composition: Pure Gases Membrane thickness: 38 - 106 μm Sulfoxide Content in Membrane: 0 – 30 wt% | Sulfoxide modified poly(vinyl alcohol) | SO ₂ , N ₂ , CO ₂ & O ₂ | α_{SO_2/N_2} : 94 – 20100 @ 2 atm | SO ₂ permeability = 14 – 1900 cm ³ (STP).cm/(cm ² .s.cmHg x10 ¹⁰ @ 1 Bar, 6 – 4960 cm ³ (STP).cm/(cm ² .s.cmHg x10 ¹⁰ @ 1.5 Bar & 0.7 – 22300 cm ³ (STP).cm/(cm ² .s.cmHg x10 ¹⁰ @ 2 Bar | (Imai <i>et al.</i> 1985:416) |
| 1988 | Pressure: 1 – 2 Bar Temperature: 19 - 24°C Gas Composition: Pure gases Membrane thickness: 45-72μm Sulfone content in membrane: 0-34.7% | Sulfone-modified poly (vinyl Alcohol) | SO ₂ , N ₂ & O ₂ | α_{SO_2/O_2} : 3500 – 9666.7 α_{SO_2/N_2} : 3500 - 29000 | SO ₂ permeability = 0.7 -2900 cm ³ (STP).cm/(cm ² .s.cmHg x10 ¹⁰ | (Imai <i>et al.</i> 1988:1817) |

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Table 2.4 State of the art SO₂ gas transport in membranes

| Year | Conditions | Membrane | Components | Ideal Selectivity | SO ₂ Permeability/ Flux | Source |
|------|---|---|--|---|---|------------------------------------|
| 1989 | Trans-membrane SO ₂ pressure: 0 – 2.4 Bar. Trans-membrane O ₂ & N ₂ pressure: 5 – 15 Bar Upstream pressure (binary permeation): 3 – 10 Bar, downstream pressure (binary permeation): 1 Bar Temperature (Binary permeation): 23°C Temperature (single permeation): 21 - 84°C Gas Composition: Pure gases (SO ₂ , N ₂ & O ₂), Binary (1.5 – 10 vol% SO ₂ balance O ₂) Membrane thickness: 10 μm | Seragel-70 | SO ₂ , N ₂ & O ₂ | α_{SO_2/O_2} : 212 α_{SO_2/N_2} : 808 | SO ₂ Permeability = 2100 mol.m.m ⁻² .s ⁻¹ .Pa | (Dytnerskii <i>et al.</i> 1989:49) |
| 1999 | SO ₂ Feed Partial pressure: 3.5 x10 ⁻⁵ - 0.2 Bar Temperature: 25 °C Gas Composition: (93ppm & 5.99% SO ₂ in N ₂) + N ₂ Membrane thickness: 100 μm | Deionised water supported on microporous poly (vinylidene difluoride) | SO ₂ & N ₂ | - | SO ₂ permeance = 6 x 10 ⁻⁴ mol.m ⁻² .s ⁻¹ .kPa ⁻¹ | (Teramoto <i>et al.</i> 1999:109) |
| 2007 | Feed Pressure: 1 Bar Trans-membrane pressure: 0.2 – 0.5 Bar Temperature: 25-45°C Gas Composition: Pure Gases Membrane thickness: 150 μm | Ionic liquid supported on Polyethersulfone | SO ₂ , N ₂ , CH ₄ & CO ₂ | α_{SO_2/CO_2} : 9 – 19 α_{SO_2/N_2} : 126 – 233 α_{SO_2/CH_4} : 87 – 124 | SO ₂ permeability = 4500 – 11900 Barrer | (Jiang <i>et al.</i> 2007:5059) |
| 2009 | Feed Pressure: Trans-membrane pressure: 0.2 – 0.5 Bar Temperature: 25-45°C Gas Composition: Pure Gases Membrane thickness: 150 μm | Ionic liquid supported on Polyethersulfone | SO ₂ , N ₂ , CH ₄ & CO ₂ | α_{SO_2/CO_2} : 7 – 19 α_{SO_2/N_2} : 126 – 337 α_{SO_2/CH_4} : 80 – 196 | SO ₂ permeability = 3750 – 9750 cm ² .s ⁻¹ .kPa ⁻¹ | (Jiang <i>et al.</i> 2009:596) |

2.4.1 SIGNIFICANCE OF SO₂ MEMBRANE SEPARATION RESEARCH

In the present study, it is intended to separate SO₂/O₂ gas mixtures through preferential permeation of SO₂ as will be outlined in Section 4.1.1. As such, the state of the art review entails studies that focus on both the pure and binary permeation of SO₂ through polymers, as it is intended to preferentially permeate SO₂.

A study performed by Zavaleta & McCandless, (1976:333) dwelt on laboratory synthesis of membrane materials for SO₂ separation and the subsequent characterization without an ultimate link to a particular industrial application. However a majority of the SO₂ separation studies underscore the importance of the elimination of SO₂ from flue gas streams through diverse technologies inclusive of membrane technology because SO₂ poses a threat to the environment (Kuehne & Friedlander, 1980a:609; Imai *et al.* 1988:1817; Seibel & McCandless, 1974:76; Pfromm & Koros, 1993:6141; Teramoto *et al.* 1999:110; Jiang *et al.* 2007:5058). Control of SO₂ atmospheric concentrations can either be done through desulphurization of the combustion gases or desulphurization of fuels to be combusted (Imai *et al.* 1988:1817; Imai *et al.* 1985:413). It is a pity though that the latter method faces difficulty when dealing with solid fuels, as such desulphurization of combustion gases remains as the feasible option. Laboratory scale studies dealing with SO₂ membrane separation have simulated conditions in industrial applications and characterized test membranes under these conditions (Seibel & McCandless, 1974:76). Kuehne & Friedlander, (1980a:609) and Imai *et al.* (1988:1817), presented the desire to develop alternative SO₂ control technologies such as membranes as they are less costly, efficient and give less impact to the environment. Yet membrane technology had facilitated the separation of gas mixtures in the 20th century, commercial industrial scale applications were dampened by the inadequate performance of membranes (Kuehne & Friedlander, 1980a:609). However, development of high flux membranes then offered promising prospects for industrial use (Kuehne & Friedlander, 1980a:609). Dytnerskii *et al.* (1989:49) and Yampolskii *et al.* (1983:1832) envisioned industrial membrane SO₂ separation as not only a technology that could inhibit atmospheric pollution from power plants, but a technology with the potential to harness valuables such as the SO₂ emitted for sulphuric acid production. Teramoto *et al.* (1999:110) underscored the need to prevent air pollution by the elimination of SO₂ from flue gases through a much simpler and energy saving technique such as supported liquid membranes with de-ionized water as the supported liquid in question. Jiang *et al.* (2007:5058), in light of the control of SO₂ emissions from the combustion of fossil fuels also proposed the use of supported liquid membranes. The

difference with the study by Teramoto *et al.* (1999:110) being that ionic liquids were the supported liquids in question. Jiang *et al.* (2007:5058) cited the stability of ionic liquids from evaporation and entrainment into the gas streams as desirable characteristics over the conventional de-ionized water.

2.4.2 SO₂ MEMBRANE SEPARATION RESEARCH OBJECTIVES

The main thrust of SO₂ membrane research has been to identify and characterize materials which would selectively allow SO₂ transport (Kuehne *et al.* 1980a:609). Manipulated variables inclusive of process temperature, process pressure, SO₂ concentrations and stage cut have been used to characterize membranes (Dytnerskii *et al.* 1989:49). A review by Felder *et al.* (1975:235) presents the effect of gas pressure, humidity, and membrane plasticization all in an effort to characterize the respective membranes for SO₂ permeation. As an additional manipulated variable, Yampolskii *et al.* (1983:1832) investigated the effect of membrane thickness on permeability. Studies involving the synthesis and characterization of membranes also investigate the effect of ingredient loading on response variables (Imai *et al.* (1988:1817); Zavaleta & McCandless, (1976:333); Imai *et al.* (1985:413); Imai *et al.* (1993:1525)). A study by Jiang *et al.* (2009:595) sought to bring to light the factors responsible in acidic gas separation through supported ionic liquid membranes.

2.4.3 SO₂ MEMBRANE SEPARATION RESEARCH APPROACH

The most adopted approach to membrane characterization for gas separation has been to investigate the effect of diverse process parameters inclusive of temperature, pressure and gas composition on both pure component and binary permeation. Ultimately, model development is performed so as to generate a relation that would aid the prediction of the gas transport behavior. In studies that seek to characterize new membrane types, a membrane synthesis stage maybe included to the approach (Imai *et al.* 1988:1817; Seibel & McCandless 1974:76; Imai *et al.* 1985:413).

Kuehne *et al.* (1980a:610) determined the pure component permeability coefficients of experimental gases through Polyacrylate and Cellulose triacetate membranes and then developed a two and three parameter model. Subsequent model predictions were then compared with actual experimental results to subject the models to examination. A similar approach was adopted by Kuehne *et al.* (1980b:616), however both pure component and binary permeation experiments were performed. Authors inclusive of Dytnerskii *et al.* (1989:49), Imai *et al.* (1988:1817), Imai *et al.* (1985:413), Zavaleta & McCandless, (1976:333) and Seibel & McCandles, (1974:76) only investigated the effect of process

parameters on gas permeation of the studied gases whilst neglecting model development. Yampolskii *et al.* (1983:1832) though did not develop a model, but determined the effect of process parameters on permeability, diffusivity and solubility of SO₂ in Polyvinyltrimethyl Silane. Comparison of results with the dual mode sorption model was then done. Model development is quite pivotal, as it allows for speculation of expected outcomes without actual experimentation. However, the model would have to be tested prior to application. Jiang *et al.* (2007:5060), after investigating the effect of process parameters, employed correlation equations to predict the permeability of SO₂ in supported ionic liquid membranes. The predicted values differed extensively from actual experimental values (Jiang *et al.* 2007:5060). Teramoto *et al.* (1999:109) determined the permeance of SO₂ in a supported liquid (water) membrane. SO₂/N₂ binary mixtures were used while varying the SO₂ feed partial pressure and membrane thickness. The gas phase mass transfer coefficient was also determined. A permeation model developed in an earlier study was employed and it accurately predicted experimental results gotten in the study by Teramoto *et al.* (1999:109).

2.4.4 SO₂ MEMBRANE SEPARATION RESEARCH FINDINGS

Based on the investigated parameters in a given study, the behavior of response variables to changes in manipulated variables may be graphed or presented in model form. Transport of SO₂ in polymeric membranes has generally presented a pressure and temperature dependant permeability, and the subsequent SO₂ selectivity in binary mixtures as such has proved to also be dependent on these parameters (Zavaleta & McCandless, 1976:348).

For the separation of SO₂ and N₂ using a sulfolane plasticised vinylidene fluoride membrane, the highest selectivities were achieved at the highest operational pressure (Seibel & McCandless, 1974:76). The SO₂ selectivity increased with sulfolane loading from 0 wt % to 8.2 wt % and then went on a downward trend with further sulfolane loading (Seibel & McCandless, 1974:77). However, the gas flux increased continually with an increase in sulfolane loading. Reduced SO₂ selectivity and increased gas flux was noted with increased operational cell temperature (Seibel & McCandless, 1974:78). The gas flux through the membrane, the percentage of SO₂ in the permeate and the separation factor increased as the SO₂ percentage in the feed was increased (Seibel & McCandless, 1974:78).

From a binary SO₂/N₂ mixture the SO₂ volume percentage in the permeate and the selectivity of seven different Polyvinylidene fluoride modified membranes inclusive of sulfolene modified Polyvinylidene fluoride proved identical (Zavaleta & McCandless, 1976:338). It is the much higher permeation rate of SO₂ in sulfolene modified Polyvinylidene

fluoride that allowed the membrane to stand out and thus be chosen for further investigation. An increase in the SO₂ pseudo-permeability coefficient was noted with the increase of sulfolene content in the Polyvinylidene fluoride modified membrane at all investigated temperatures. High SO₂ permeability coefficients were gotten at low temperatures (Zavaleta & McCandless, 1976:340). N₂ pseudo-permeability coefficients increased with increasing temperature and weakly depended on sulfolene content which presented a great potential for use of the membrane in question for SO₂/N₂ separation. However, a vital realization was that, whilst the SO₂ pseudo-permeability coefficient increased with sulfone content, a sulfone content of 18 wt % offered the best overall performance. Greater sulfone percentages resulted in pinhole development at higher process temperatures. The pure component permeability coefficient of SO₂ in 18 wt % Polyvinylidene fluoride increased with increasing process pressure and decreasing process temperature. With the background that the permeability coefficient is a product of diffusivity and solubility, the SO₂ permeability behavior in the system was thus described as a solubility controlled permeation process. The latter description was based on the fact that gas solubility in a polymer generally increases with decreasing temperature and the vice-versa is true for diffusivity (Zavaleta & McCandless, 1976:341). The permeability of both O₂ and N₂ presented a diffusivity controlled form in sulfone modified Polyvinylidene fluoride. O₂ permeability depended slightly on pressure, and increased with temperature, whilst N₂ permeability was independent of pressure and increased with temperature (Zavaleta & McCandless, 1976:342). In the binary separation of SO₂ from N₂, the N₂ pseudo-permeability coefficient was greater than the pure component permeability coefficient at low temperatures, which signified the presence of gas-gas and gas-polymer interactions in the SO₂/N₂ mixture. Thus N₂ transport in the sulfone modified Polyvinylidene fluoride membrane depended on the amount of SO₂ sorbed in the polymer. The SO₂ sorbed in the polymer was high at low temperatures (Zavaleta & McCandless, 1976:345). With increasing temperature the sorbed SO₂ decreased and the N₂ pseudo-permeability then adopted the lower N₂ pure component permeability behavior (Zavaleta & McCandless, 1976:350). In a similar manner, the SO₂ separation factor increased with decreasing temperature and decreased with increasing temperature (Zavaleta & McCandless, 1976:350).

Two studies by Kuehne & Friedlander, (1980a:613) and Kuehne & Friedlander, (1980b:616) proved pure SO₂ permeability to increase rapidly with increasing downstream and upstream pressures in Polyacrylate, Cellulose Triacetate and Polyacrylate/Cellulose Triacetate composite membranes. However, the SO₂ solubility in Polyacrylate proved to depend weakly on pressure (Kuehne & Friedlander, 1980a:614). The composite membranes exhibited a

great potential of concentrating SO₂ in dilute mixtures with N₂ and significant SO₂ – N₂ gas interactions were suspected to dominate the binary transport behaviour (Kuehne & Friedlander, 1980b:622). Though the performance of these composite membranes proved superior to earlier membranes synthesized for SO₂ separation, they still were deemed unsuitable for combustion gas cleaning due to low flux values (Kuehne & Friedlander, 1980b:622).

SO₂ flux and permeability in the glassy polymer Polyvinyltrimethyl Silane presented two distinct behaviours at low (< 100 kPa) and high (100 KPa – 300 Kpa) upstream pressures (Yampolskii *et al.* 1983:1832). Only in the high pressure range did the SO₂ permeability and flux increase linearly with pressure, otherwise weak dependence on pressure was observed at the low pressure range. SO₂ permeability in PVTMS increased with temperature only up to a maximum at high operational pressures (≥ 0.22 MPa) and then decreased. At lower operational pressures (≤ 0.16 MPa) SO₂ permeability decreased continuously with temperature (Yampolskii *et al.* 1983:1834).

In a study by Imai *et al.* (1985:413), the permeation of SO₂ through sulfoxide modified poly (vinyl alcohol) membranes depended on both, sulfoxide compositions and the differing alkyl substituents. An exponential increase of the SO₂ permeability was observed with an increase in sulfoxide content (from 10% -30%) in the poly (vinyl alcohol) membrane. Much bulkier alkyl substituents in the polymer chain also enhanced the SO₂ permeability. Ultimately, the SO₂ permeability also increased with increasing applied feed pressure. As such, for any given sulfoxide composition and with every alkyl group, SO₂ permeability increased with applied pressure. On the contrary, O₂ and N₂ pure component permeability coefficients were independent of applied pressure and weakly depended on the alkyl group present in the polymer chain. Based on the presented transport behavior of SO₂, O₂ and N₂, there was great potential for use of the modified sulfoxide poly (vinyl alcohol) membranes in the elimination of SO₂ from combustion gas mixtures (Imai *et al.* 1985:413).

The presence of sulfone in modified Poly (vinyl Alcohol) facilitated the transport of SO₂ through the polymer and the SO₂ permeability coefficient increased with increasing sulfone content (Imai *et al.* 1988:1827). Bulkier alkyl substituents in the modified poly (vinyl Alcohol) polymer proved to increase SO₂ permeability. SO₂ permeability also increased with increased process pressure (Imai *et al.* 1988:1827). A striking fact is that the pure component N₂ and O₂ permeabilities were unaffected by both sulfone content and pressure. The latter statement gives a plus to sulfone based membranes for the separation of SO₂ from either N₂ or O₂.

The Seragel based membranes investigated by Dytnerskii *et al.* (1989:49) exhibited pressure dependant permeabilities of both SO₂ and O₂. Pure component permeabilities of both gases increased with an increase in pressure. However a net decrease in SO₂ permeability was noted with an increase of process temperature which was attributed to a drastic decrease in SO₂ solubility in the polymer with temperature despite the increase of diffusivity with temperature. SO₂ present in dilute amounts in mixtures with O₂ was concentrated by the Seragel based membranes, and the SO₂ concentration in the permeate increased with increasing feed side gas velocity Dytnerskii *et al.* (1989:53).

Similar results to those gotten by Imai *et al.* (1985:413) were gotten by Imai *et al.* (1993:1525), increased SO₂ permeability was observed with increased bulkiness of substituents in the Sulfoxide - modified Poly (Vinyl Alcohol) membrane. The SO₂/N₂ selectivity reached maxima at 23.5 % sulfoxide content as sulfoxide content was increased in the polymer whilst the SO₂ permeability increased gradually with increasing sulfoxide content (Imai *et al.* 1993:1528). The maxima observed on the SO₂/N₂ separation factor was thought to be a result of a competition of SO₂ and N₂ transport across the membrane attributed to SO₂ plasticization/swelling of the polymer at high sulfoxide contents (Imai *et al.* 1993:1528). Though sulfoxide-modified cellulose membranes offered high SO₂/N₂ separabilities, sulfoxide modified Poly (Vinyl Alcohol) offered much superior SO₂/N₂ separabilities (Imai *et al.* 1993:1529).

A SO₂ sorption study in Polysulfone was conducted by Pfromm & Koros, (1993:6141), and the resultant outcomes were used to estimate the expected SO₂/N₂ behavior of a 1 % SO₂ in N₂ mixture. The solubility of the SO₂ molecule in polysulfone far exceeded that of N₂ and CO₂, such that the solubility selectivity ($S_{SO_2}/S_{N_2} = 694.13$) was very large, but was quenched by the diffusivity selectivity ($D_{SO_2}/D_{N_2} = 0.12$) that favored the N₂ molecule. Thus the overall estimated selectivity was then given as a product of two selectivity contributions.

The permeance of SO₂ in micro porous poly (vinylidene difluoride) impregnated with de-ionized water presented a behavior that was contrary to that observed in non-porous polymeric membranes (Teramoto *et al.* 1999:114). As the SO₂ partial pressure in the feed stream increased from 3.5 Pa to 0.55 kPa, the corresponding permeance decreased exceedingly, about six times (Teramoto *et al.* 1999:115)! SO₂ permeance also decreased with increasing membrane thickness (Teramoto *et al.* 1999:115). Conversely the SO₂ partial pressure in the retentate and sweep gas stream increased with SO₂ partial pressure in the feed. The desirable feature of the permeance behavior presented by the supported liquid membrane was the high SO₂/N₂ selectivity of more than 10 000 at low feed SO₂ partial

pressures of 10^{-3} to 10^{-2} kPa which was not possible with non-porous polymeric membranes (Teramoto *et al.* 1999:117). The latter characteristic of the supported liquid membrane made the membrane ideal for flue gas desulphurization processes that often have low SO₂ partial pressures (Teramoto *et al.* 1999:118).

The SO₂ permeability in five imidazolium based ionic liquids ([emim][BF₄], [bmim][Tf₂N], [bmim][BF₄], [hmim][BF₄] and [bmim][PF₆]) supported on Polyethersulfone membranes studied by Jiang *et al.* (2007:5058) decreased with increasing ionic liquid viscosity ([emim][BF₄] < [bmim][Tf₂N] < [bmim][BF₄] < [hmim][BF₄] < [bmim][PF₆]). The permeability proved to be diffusion controlled rather than solubility controlled. The solubilities of SO₂ in two ionic liquids ([emim][BF₄] and [bmim][PF₆]) that presented vastly differing SO₂ permeabilities (9350 Barrer and 5200 Barrer respectively) were almost similar. The different permeabilities were thus attributed to differing diffusivities since permeability is a product of solubility and diffusivity. The diffusivity through the ionic liquids was presented as a function of both viscosity and density, and the differing densities and viscosities of ionic liquids then gave an explanation for the difference in permeabilities. However a quantitative approach to the study over estimated the experimental results as such further research was deemed due. The increase of SO₂ permeability in [bmim][Tf₂N] at 25 °C by 1206 Barrer with slight increases in trans-membrane pressure from 10 to 50 kPa and the negligible change in CO₂ permeability under the same conditions made this technology promising for SO₂ recovery from flue gases. SO₂ permeability in [bmim][Tf₂N] also increased with temperature.

A follow up study by Jiang *et al.* (2009:596) also affirms the potential for SO₂ separation through the use of supported ionic liquid membranes. The latter statement is based on the fact that the CO₂ permeability in the SILMs remains almost constant with an increase in trans-membrane pressure, whilst that of SO₂ increases with a trans-membrane pressure increase. Also, the permeability of simple gases inclusive of N₂ and CH₄ proved to be over a magnitude less than acidic gases of which SO₂ is one. Several ionic liquid cation-anion matchings were performed and the anions [BF₄]⁻ and [CF₃SO₃]⁻ presented great capability of separating SO₂ from CO₂, N₂ and CH₄. Increasing temperature was found to decrease the ideal selectivities of all gas pairs through [emim][CF₃SO₃] whilst operational pressure weakly affected the ideal selectivities.

2.5 GENERAL REVIEW OF SO₂ SEPARATION THROUGH MEMBRANES

From the presented studies, the general trend with time has been the shift of focus towards facilitated transport membrane types that have liquids supported on micro-porous polymeric

membranes. The task of the liquids being to shuttle selected gas molecules across the membrane barrier. The Sulfone based membranes presented in the current review prove to possess a great potential of separating SO₂ from gas mixtures. It's a pity though that by the end of the 20th century, they still found no commercial application. Polysulfone, an alternative sulfone based polymer however was already employed on a commercial scale by Air products in the 20th century for hydrogen recovery from ammonia purge gas streams (Baker, 2002:1393).

A perfect explanation of the non-commercialization of membranes reported in academic research is given by Baker, (2002:1393). Baker, (2002:1393) reports that just about eight or nine polymeric membranes (Polysulfone, Polyimide/Polyaramide, Polyimide, tetrabromo Polycarbonate, Cellulose acetate, Polyphenylene oxide and Silicone rubber) had found commercial application by the end of the 20th century despite the availability of hundreds of polymers that had been reported to have much higher selectivities and permeabilities. Several other criteria are pivotal for commercialization besides permeability and selectivity. The ability of the polymer to be spun economically into stable thin films, chemical and thermal resistance, resistance to plasticization and aging (Baker, 2002:1393; Brunetti *et al.* 2011:286). The explanation by Baker, (2002:1393) aids in narrowing the search for gas separation membranes for given applications.

Presented authors in the state of the art review inclusive of Seibel & McCandless, (1974:76), Imai *et al.* (1988:1817) and Zavaleta & McCandless, (1976:333) have brought to light that Sulfone based membranes have a great SO₂ separating potential. The latter fact presents a basis upon which to select commercial membranes for the current application (SO₂/O₂ separation). Taking up from where they left, the gap intended to be bridged by the current study is the characterization of commercial membranes, considering the SO₂/O₂ binary system.

Despite the presentation of diverse studies in the SO₂ field of membrane gas separation in the present review, one study by Dytnerkii *et al.* (1989:49) considered polymeric membrane separation of SO₂ in the SO₂/O₂ binary system. The rest of the presented studies focused on individual gas transport of SO₂ and also considered SO₂ gas separations in other binary systems involving SO₂ but not with O₂. In the study by Dytnerkii *et al.* (1989:49), little focus was given to the binary study and the membrane in question is still non-commercial.

2.6 REFERENCES

- [1] BAKER, R.W. 2002. Future directions of membrane gas separation technology. *Industrial & Engineering Chemistry Research*, 41:1393-1411.
- [2] BAKER, R.W. 2008. Vapor 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.)
- [3] BRUNETTI, A., BARBIERI, 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*. UK: Royal Society of Chemistry. p.284-323.)
- [4] DHINGRA, S.S. 1997. Mixed Gas Transport Study through Polymeric Membranes: A Novel Technique. Blacksburg, Virginia:V.P.I.S.U. (Dissertation – Phd) 173p.
- [5] DYTNEK, Y.I., KAGRAMANOV, G.G., STOROZHUK, I.P. & KOVALENKO, N.F. 1988. SO₂ Separation from Gaseous Mixtures by Membranes. *Journal of Membrane Science*, 41:49-54, 8 Mar.
- [6] FELDER, R.M., SPENCE, R.D. & FERELL, J.K. 1975. Permeation of Sulphur Dioxide Through Polymers. *Journal of Chemical and Engineering Data*, 20(3):235-242.
- [7] 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.)
- [8] IMAI, K., SHIOMI, T., TEZUKA, Y. & SATOH, M. 1985. Selective permeation of sulphur dioxide through sulfoxide modified poly(vinyl alcohol) membranes. *Macromol*, 6:413-418, 14 Feb.
- [9] IMAI, K., SHIOMI, T., TEZUKA, Y. & TAKADA, M. 1988. Synthesis of sulfone-modified poly(vinyl alcohol) and its application for permselective membrane for sulphur dioxide. *Journal of Applied Polymer Science*, 35:1817-1828, 30 Jul.
- [10] IMAI, K., SHIOMI, T., TEZUKA, Y., ITAMOUCHI H. & MIYA, M. 1993. Separability of SO₂ from SO₂/N₂ mixture through sulfoxide-modified poly(vinyl alcohol) and cellulose membranes. *Journal of Applied Polymer Science*, 48(9):1525-1529, 14 Aug.
- [11] INNOVATIVE GAS SYSTEMS. 2011. Gas separation, purification and recovery. <http://www.igs-global.com/gas-separation-purification-and-recovery.htm> Date of access: 21 Dec 2011.
- [12] JIANG, Y., ZHOU, Z., JIAO, Z., LI, L., WU, Y. & ZHANG, Z. 2007. SO₂ Gas Separation Using Supported Ionic Liquid Membranes. *The Journal of Physical Chemistry*, 111(19):5058-5061, 3 Apr.

- [13] JIANG, Y., ZHOU, Z., JIAO, Z., LI, L., WU, Y. & ZHANG, Z. 2009. Permeability and selectivity of sulphur dioxide and carbon dioxide in supported ionic liquid membranes. *Chinese Journal of Chemical Engineering*, 17(4):594-601, 3 Mar.
- [14] KHOLODOVYCH, V. & WELSH, W.J. 2007. Densities of amorphous and crystalline polymers. (In Mark, J.E., ed. *Physical Properties of Polymers Handbook*. New York: Springer. p.611-617.)
- [15] 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.)
- [16] KUEHNE, D.L. & FRIEDLANDER, S.K. 1980a. Selective Transport of Sulphur Dioxide through Polymer Membranes. 1 Polyacrylate and Cellulose Triacetate Single Layer Membranes. *Industrial & Engineering Chemistry Process Design and Development*, 19(4):609-616.
- [17] KUEHNE, D.L. & FRIEDLANDER, S.K. 1980b. Selective transport of sulphur dioxide through polymer membranes. 2. Cellulose Triacetate/Polyacrylate composite membranes. *Industrial & Engineering Chemistry Process Design and Development*, 19:616-623.
- [18] MALYKH, O.V., GOLUB, A.Y. & TEPLYAKOV, V.V. 2010. Polymeric membrane materials: New aspects of empirical approaches to prediction of gas permeability parameters in relation to permanent gases, linear lower hydrocarbons and some toxic gases. *Advances in Colloid and Interface Science*, 164:89-99, 27 Oct.
- [19] 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.D., eds. *Materials science of membranes for gas and vapor separation*. Chichester: John Wiley & Sons. p.1 - 47.)
- [20] PANDEY, P. & CHAUHAN R.S. 2001. Membranes for gas separation. *Progress in Polymer Science*, 26:853-893, 2 Mar.
- [21] 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.)
- [22] PAUL, D.R. & YAMPOL'SKII, Y.P. 1994. Introduction and perspective. (In Paul, D.R. & Yampol'skii, Y.P., eds. *Polymeric Gas Separation Membranes*. Florida: CRC Press. p. 1-15. http://www.amazon.com/dp/0849344158/ref=rdr_ext_tmb#reader_0849344158 Date of access 20 May 2010.
- [23] PFROMM, P.H. & KOROS, W.J. 1993. Sorption and Transport of Sulphur Dioxide in Polysulfone. *Macromolecules*, 26:6141-6142.
- [24] ROBESON. 1999. Polymer membranes for gas separation. *Current Opinoin in Solid State and Material Science*, 4: 549-552.

- [25] SEIBEL, D.R. & McCANDLESS, F.P. 1974. Separation of sulphur dioxide and nitrogen by permeation through a sulfolane plasticized vinylidene fluoride film. *Industrial & Engineering Chemistry Process Design and Development*, 13(1):76-78, 19 Sept.
- [26] STERN, S.A & FRIED, J.R. 2007. Permeability of polymers to gases and vapors. (In Mark, J.E., ed. *Physical properties of polymers handbook*. New York: Springer. p.1033-1047.)
- [27] TERAMOTO, M., HUANG, Q., MAKI, T. & MATSUYAMA H. 1999. Facilitated transport of SO₂ through supported liquid membrane using water as a carrier. *Separation and Purification Technology*, 16:109-118, 9 Nov.
- [28] UNITED STATES OF AMERICA. Department of Energy. 2005. Energy tips – process heating: Process heating tip sheet #3. 2p.
http://www1.eere.energy.gov/manufacturing/tech_deployment/pdfs/oxygen_enriched_combustion_process_htgts3.pdf Date of access : 21 Dec 2011.
- [29] YAMPOL'SKII, Y.P., VOLKOV V.V., KALYUZHNYI, N.E. & DURGAR'YAN, S.G. 1983. Permeability, Diffusion and Sorption of SO₂ in Polyvinyltrimethyl Silane Membranes. *Polymer Science U.S.S.R.*, 26(8):1832-1840, 3 Feb.
- [30] ZAVALETA, R. & McCANDLESS, F.P. 1976. Selective permeation through modified polyvinylidene fluoride membranes. *Journal of Membrane Science*, 1:333-353, 29 Mar.