



A Dual-mode model interpretation of CO₂/CH₄ permeability in polysulfone membranes at low pressures

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ABSTRACT

An asymmetric membrane of polysulfone (PSf) was synthesized by phase inversion method. Permeation experiments were carried out between 2 to 5 bar pressure, and at temperatures 20 to 45°C. The dense-selective layer of PSf membrane presents regular thickness (about 5 μm), and was not possible to observe the formation of macrovoids in porous layer. The CO₂ permeability through membrane was 18.8 Barrer at 35°C and 2 bar pressure, and this relationship between the pressure and the CO₂ permeability was described adequately by Dual-mode model. The absence of CH₄ permeability at 2 and 3 bar pressure, qualifies the PSf membrane for gases separation with high selectivity in this range.

Key words: asymmetric membranes, CO₂/CH₄ permeability, Dual-mode model, polysulfone.

INTRODUCTION

Currently, there is a need in the world to substitute fossil fuels for renewable sources in the energy production. Natural gas has significant advantages over other fossil fuels, in particular the reduction in atmospheric emissions from their combustion. Concentrations of sulfur oxides (SO_x) and particulate matter are low in flue gas produced by natural gas combustion.

Biogas consists mainly of methane (CH₄), carbon dioxide (CO₂) and water (H₂O), having other trace compounds (H₂S, siloxane, VOC's, NH₃, O₂, CO and N₂) in its composition. Biogas is a combination of chemical species produced in the organic matter degradation process. Biogas is

produced in landfills, anaerobic reactors, pyrolysis reactors, among others. The use of methane, present in biogas, is a renewable alternative instead of using natural gas in its various applications. The biomethane is obtained from the removal of carbon dioxide and water, besides trace components present in the biogas, and has in its composition from 95 % to 97 % (vol/vol) of methane (Krich et al. 2005, Ryckebosch et al. 2011, Chen et al. 2015). Within this context, polymeric membranes for methane gas purify, have received great attention due to several advantages, such as energy efficiency in operation and low environmental impact regarding to other technologies (Basu et al. 2010a). Polymeric membranes have been studied for separating CO₂ (Wang et al. 2002, Qin et al. 2005, Husken et al. 2010, Minelli et al. 2013, Saedi et al. 2013). One of the most investigated polymers

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(Hu et al. 2003, Ismail and Lai 2004, Gabelman and Hwang 2005, Aroon et al. 2010, Scholes et al. 2010, 2012, Julian and Wenten 2012, Hölck et al. 2013, Robeson et al. 2014, Chen et al. 2015) for the separation of CO₂ is polysulfone (PSf). PSf has low cost regarding to others high performance polymers, has high chemical resistance (acid, alkali, salt solutions, detergents, oils and alcohols) and good mechanical properties. Blends of PSf with others polymers and inorganic materials have being also evaluated for the separation of CO₂ (Qin and Chung 2006, Ahn et al. 2008, Basu et al. 2010b, Deng and Hägg 2010, Rafiq et al. 2012, Eiras et al. 2016). The phase inversion is a process widely used for the synthesis of polymeric membranes. Several solvents (McHattie et al. 1991, Ghosal et al. 1996, Feng et al. 2002, Wang et al. 2002, Hu et al. 2003, Ismail and Hassan 2006, Conesa et al. 2007, Ahn et al. 2008, Chakrabarty et al. 2008, Kim and Marand 2008, Aroon et al. 2010) have being used in the synthesis of polymeric membranes: 1-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), N,N'-dimethylacetamide (DMAc), hexamethylphosphoramide (HMPA), trimethylphosphate (TMP), triethylphosphate (TEP), N,N'-dimethylformamide (DMF), chloroform and methylene chloride.

However, few studies are reported in the literature for the separation of CO₂ from PSf membranes at low pressures (up to 5 bar) as well as data on the influence of temperature on the performance of the separation process.

In the present work, a detailed study on the performance of a PSf membrane for the separation of CO₂ in a range of low pressure and different temperatures was performed.

MATERIALS AND METHODS

PREPARATION OF ASYMMETRIC MEMBRANES

The preparation of PSf membrane was conducted according to the phase inversion process by

immersion-precipitation method (Godinho et al. 2016). PSf (30 %) used in the membrane synthesis was supplied by Sigma-Aldrich in the form of pellets and molecular weight of 35,000 g mol⁻¹. The solvents used in the synthesis were N, N'-dimethylformamide (DMF) and 1-methyl-2-pyrrolidone (NMP), molar mass of 73.1 g mol⁻¹ and 99.13 g mol⁻¹, respectively, with saturation pressure of 2.7 mmHg (DMF) and 0.29 mmHg (NMP) at 20°C. Distilled water and analytical standard ethyl alcohol were used as non-solvent in the synthesis. The gases (CO₂ and CH₄) used in the permeation tests have 99.99 % purity, supplied by Air Products.

CHARACTERIZATION AND GAS TRANSPORT MEASUREMENTS

CO₂ and CH₄ pure were singly tested under varying conditions of pressure (from 2 to 5 bar) and temperature (from 20 to 45°C), in triplicate according to the Figure 1. In order to avoid the hysteretic effects that can be caused by exposure to high-pressure gases, a procedure to avoid time dependence was conducted. After the membrane installation in the permeation cell, it has been subjected to a CO₂ flux for a period of 3 hours at a 5 bar pressure, 20°C temperature and 1 L min⁻¹ flow rate. The permeation tests were performed on the pressure range from 2 to 5 bar, and temperatures from 20 to 45°C. The gas stream (feed) is introduced into the permeation cell (Figure 1:6) perpendicularly, and the concentrated gas stream (discard), flows tangentially into the permeation cell. The permeate gas flow is measured by bolhometer (Figure 1:7) as a time (stopwatch) function. The pressure and flow of the concentrated stream were also monitored. The interval time between each triplicate point was 20 min, for each temperature worked at each pressure. For each triplicate point, six measures were performed with fixed volume and recording the time of each measurement. If the time difference between any of the averages varied between 2 and 5 s, the measurements were restarted. After all, with both gases, the membranes were again subjected to the test from 2 to 5 bar of pressure with temperature

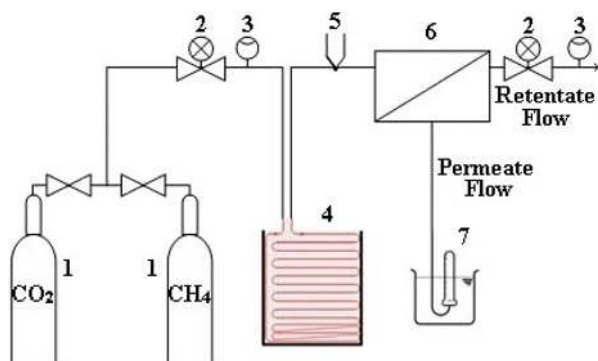


Figure 1 - Gas Permeation System. 1 – Feed gas cylinder; 2 – Pressure controller valve; 3 – Rotameter; 4 – Thermostatic bath; 5 – Thermocouple; 6 – Permeation cell; 7 – Soap bubble flow meter.

to 20°C, in order to identify possible deviations. Significant reductions (up to 70 %) were observed in permeability during the procedure.

Scanning Electron Microscopy (SEM) using a Shimadzu, model SSX-550 was used to examine the morphology and thickness of the membranes. Samples were fractured in liquid nitrogen and metalized with a thin gold layer by sputtering process with an exposure time of 2 min.

RESULTS AND DISCUSSION

PERMEATION PROPERTIES OF SINGLE PURE GASES

In a system where a gas diffuses through a membrane, the flux is usually described by Equation 1:

$$J_i = \frac{P_i}{l} (P_a - P_p) \quad (1)$$

where: J_i is the flux of specie i ($\text{m}^3(\text{STP}) \cdot \text{m}^{-2} \cdot \text{h}^{-1}$), P_i is the permeability of specie i ($\text{m}^3(\text{STP}) \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$), P_a and P_p - are the pressures in the feed and permeate (bar) and l is the membrane thickness (m).

The permeability in nonporous dense polymeric membranes can be described by the solution-diffusion mechanism, described by Equation 2 (Pauly 1999, Chen et al. 2015):

$$P = DS \quad (2)$$

where: D is the diffusivity coefficient ($\text{m}^2 \cdot \text{s}^{-1}$) and S is the solubility coefficient ($\text{m}^3(\text{STP}) \cdot \text{m}^{-3} \text{ polymer}$).

According to Arrhenius equation, the permeability (P) of a gas in a polymer is related to the temperature over the activation energy of permeation (E_p) and can be expressed according to Equation 3.

$$P = P_0 \exp \frac{-E_p}{RT} \quad (3)$$

where: P_0 is the pre-exponential factor (Barrer), and E_p is the activation energy of permeation ($\text{kJ} \cdot \text{mol}^{-1}$).

The membrane ability to separate two gases (i and j) is the ratio of their permeability, known by selectivity (α_{ij}), and represented by Equation 4.

$$\alpha_{ij} = \frac{P_i}{P_j} \quad (4)$$

Relationship between pressure and the gas permeability through the PSf membrane is shown in Figure 2.

The permeability observed for the PSf membranes are typical for CO₂ separation, where the gas transport control occurs in the dense layer (solution-diffusion mechanism). McHattie et al. (1991) obtained results of CO₂ permeability in a PSf membrane similar, i.e., a smooth reduction in permeability with increasing pressure. This behavior is typical for the Dual-mode model, since the permeability of a gas molecules is dependent of the free volume available in the polymer matrix and the gas condensability (Langmuir mode), as well as, the gas-polymer interaction (Henry's mode). However, under low pressures (2 and 3 bar), the Langmuir mode preferentially governs the transport mechanism, favoring the permeability of CO₂, to CH₄, due to its kinetic diameter, 3.3 Å and 3.8 Å respectively, until free volume saturation. From increment operating pressure, the Henry's mode preferentially governs

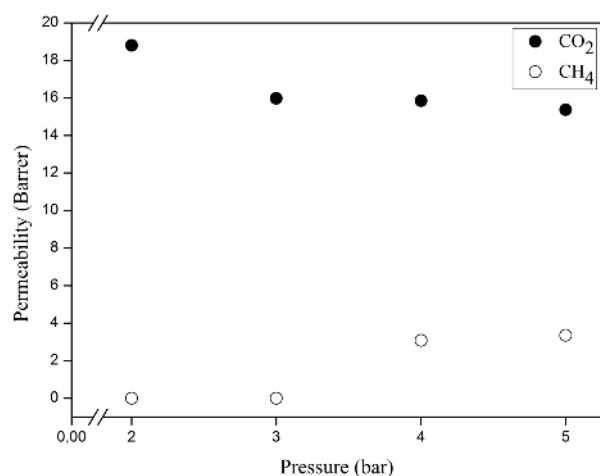


Figure 2 - Membrane permeability as a function of pressure at 35°C.

the transport mechanism, favoring the permeability of CH₄ to CO₂, since those larger molecules are generally more condensable, increasing the gas-polymer interaction. Selectivity at 3 and 4 bar were 5.1 and 4.6, respectively. It was not observed CH₄ permeability for 2 and 3 bar pressures, while between 3 and 4 bar there was a little increased in your permeability. Absence of CH₄ permeability was observed for all temperatures evaluated. Such lack of permeability may be related to free volume in the selective layer of the membrane. In general, a polymer with a low free volume fraction has a high degree of crystallinity (Sweed 2011). According Kholodovych and Welsh (2007) polymer chains are more packed in the crystalline region than in the amorphous regions of the polymer, and consequently the density of the crystalline region is larger than in the amorphous region. The molecular orientation may also have been caused during the spreading of the polymeric solution during synthesis by phase inversion process, causing an increase in the degree of crystallinity of the polymer. Given that there was no methane permeability between 2 and 3 bar, it is a region suitable for the gases separation. Figure 3 shows the SEM photomicrograph of the PSF membrane cross section.

The dense-selective layer shows regular thickness along the membrane (about 5 μm), while its total thickness is approximately 90 μm. On the porous layer of the membrane is not possible to observe the formation of macrovoids.

Figure 4 shows the temperature effect on CO₂ permeability.

The activation energies of CO₂ permeation in the membrane were 6.89, 5.52, 5.24 and 5.09 kJ·mol⁻¹ for feed pressures of 2, 3, 4 and 5 bar, respectively. Permeability increases with increasing temperature for all pressures evaluated. Such behavior is expected below of glass transition temperature of the polymer (T_g = 186°C). The activation energy of CO₂ permeation indicates affinity between CO₂ molecules and the membrane. Therefore, the activation energies obtained indicated a decreasing affinity between CO₂ molecules and the membrane, as increases pressure. Decreased activation energy with increased pressure is an indicative of the larger contribution of solubility to the permeation mechanism at higher pressures (Godinho et al. 2016).

DUAL-MODE ANALYSIS

According to the Dual-mode model, gas sorption in glassy polymers can be described as a function of pressure by Equation 5:

$$C = C_D + C_H = K_D P_a + \frac{C'_H b}{1 + b P_a} P_a \quad (5)$$

where: C_D (cm³(STP)·cm⁻³) and C_H (cm³(STP)·cm⁻³) represent Henry's Law mode sorption and Langmuir mode sorption, respectively. The parameter k_D is the Henry's law solubility coefficient, (cm³(STP)·cm⁻³), C'_H is the Langmuir sorption capacity (cm³(STP)·cm⁻³), b is an affinity parameter characterizing the ratio constants for sorption and desorption (atm⁻¹) and P_a is the feed pressure.

There is a diffusion constant associated with each mode sorption (Henry and Langmuir), considering the existence of permanent spaces

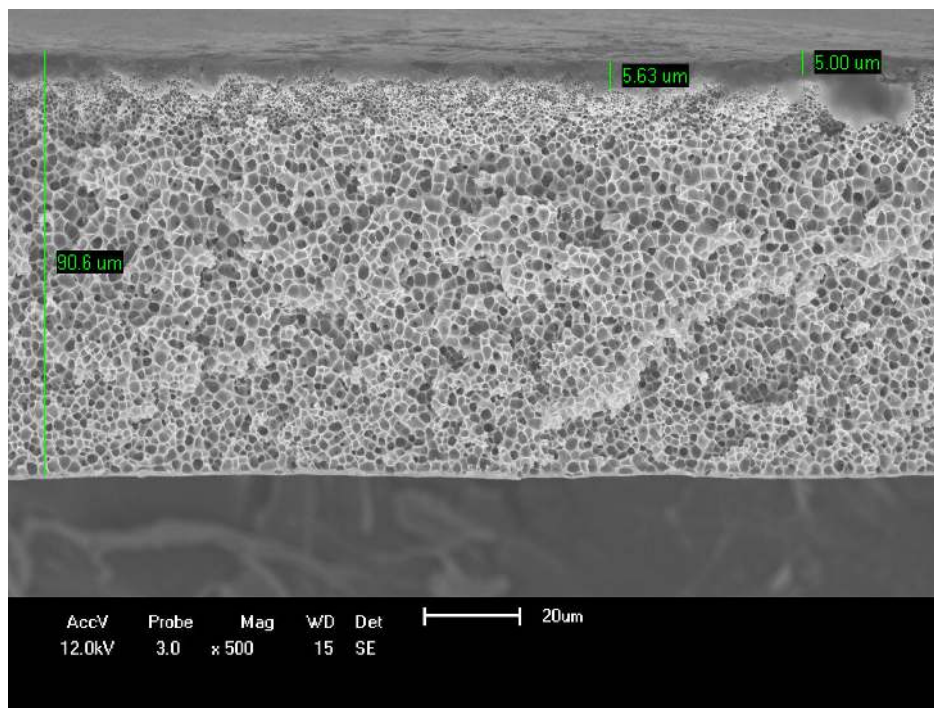


Figure 3 - Scanning electron micrograph of cross section membrane.

between polymer chains (interstitial free volume), and transient due to thermal movement of the material (Koros et al. 1976, 1978, Kanehashi and Nagai 2005). Permeability (P) can be represented as the sum of the Henry's mode and the Langmuir mode as described in Equation 6:

$$P = k_D D_D + \left(1 + \frac{FK}{1+b.P_2} \right) \quad (6)$$

$$K = \frac{c'_H b}{K_D} \quad F = \frac{D_H}{D_D}$$

where: D_H is the diffusivity coefficient regarding to Langmuir mode and D_D is the diffusivity coefficient regarding to Henry's Law mode.

Permeability obtained for the PSf membrane was evaluated in the Dual-mode model. For this purpose, model constants obtained by other authors (McHattie et al. 1991, Hu et al. 2003, Scholes et al. 2010) for the CO₂ permeation in PSf membranes were used. The constants were obtained at 35°C, and are presented in Table I.

Figure 5 shows the experimental permeability obtained in this work, and the results predicted by the Dual-mode model. The membrane used in this work was synthesized from two solvents (DMF/NMP), while constants used for the Dual-mode model were derived from different solvents. The experimental permeability was higher than those predicted from Dual-mode model, although behavior of permeability as function pressure was similar to that predicted by the model, suggesting that gas transport in the membrane is controlled in the dense-selective layer according to the Henry's and Langmuir models.

SOLUBILITY AND DIFFUSIVITY CONTRIBUTIONS

Robeson et al. 2014 established empirical equations 7 and 8 to correlate the solubility (S) and diffusivity (D) coefficients to permeability (P) in glassy polymeric membranes, obtained from permeation tests of CO₂ at temperatures from 25 to 35°C at 2 bar.

TABLE I
Dual-mode model constants for CO₂ permeation in PSf membranes.

Parameter	McHattie et al.1991	Scholes et al.2010	Hu et al. 2003		
$K_D \left(\frac{\text{cm}^3(\text{STP})}{\text{cm}^3(\text{polymer}) \cdot \text{atm}} \right)$	0.728	0.41	0.58	0.60	0.62
$C'_H \left(\frac{\text{cm}^3(\text{STP})}{\text{cm}^3(\text{polymer})} \right)$	19.6	16.2	12	10.3	8.2
$b \left(\frac{1}{\text{atm}} \right)$	0.26	0.38	0.37	0.37	0.37
$D_{D'} \left(\frac{\text{cm}^2}{\text{s}} \right)$	$4.64 \cdot 10^{-8}$	$1.10 \cdot 10^{-7}$	$1.2 \cdot 10^{-7}$	$1.09 \cdot 10^{-7}$	$6.60 \cdot 10^{-7}$
$D_{H'} \left(\frac{\text{cm}^2}{\text{s}} \right)$	$5.75 \cdot 10^{-9}$	$7.30 \cdot 10^{-9}$	$6.00 \cdot 10^{-9}$	$7.00 \cdot 10^{-9}$	$9.00 \cdot 10^{-9}$
Solvent	Dichloromethane	Chloroform	Chloroform	DMAc	NMP

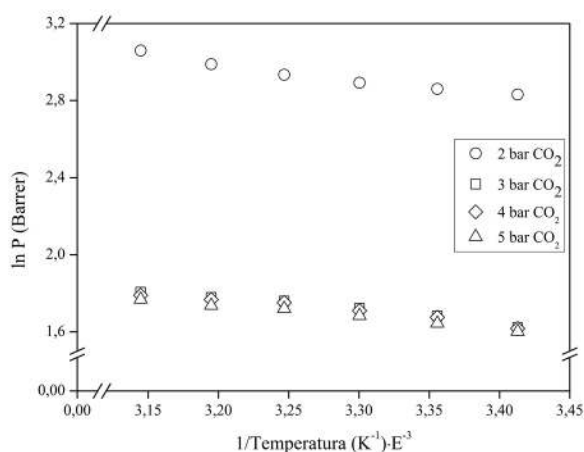


Figure 4 - Membrane permeability of CO₂ as a temperature function under varying feed pressures.

$$S_{\text{CO}_2} = 2,40 \cdot P_{\text{CO}_2}^{0,182}; R^2 = 0,441 \quad (7)$$

$$D_{\text{CO}_2} = 0,416 \cdot P_{\text{CO}_2}^{0,818}; R^2 = 0,946 \quad (8)$$

where: S_{CO_2} is the solubility coefficient of CO₂ (cm³ (STP)·cm⁻³), D_{CO_2} is the diffusivity coefficient of CO₂ (cm²·s⁻¹), and P_{CO_2} is the permeability coefficient of CO₂ (cm³(STP)·cm·cm⁻²·s⁻¹·cmHg⁻¹).

Permeabilities obtained in this work were applied to the equations, in order to estimate the diffusivity and solubility coefficients for

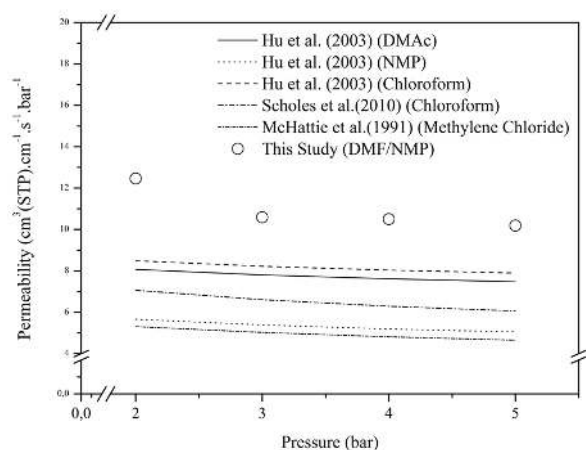


Figure 5 - Permeability predicted by the Dual-mode model in PSf membranes for CO₂ permeation at 35°C.

PSf membrane. Figure 6 shows the solubility coefficients for the PSf membrane.

There was a significant increase in the solubility coefficient with increasing pressure. Wang and Kamiya (1995), Scholes et al. (2010) and Li et al. (2014) observed a similar trend in their studies. The solubility coefficient is influenced by gas condensability, interactions between polymer and gas and the free volume in the polymeric matrix. The gas condensability increases with increasing its critical temperature, consequently increasing the solubility coefficient. The saturation temperature

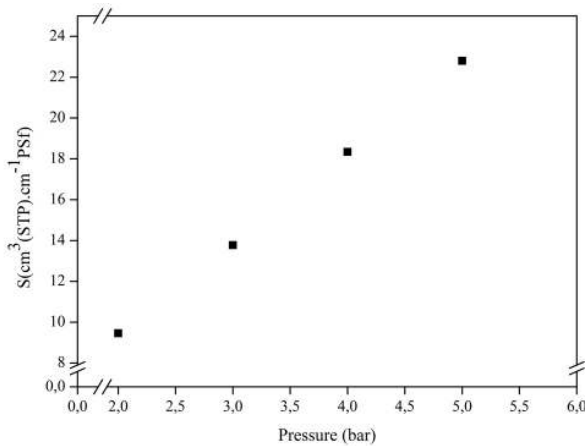


Figure 6 - CO₂ solubility coefficient in PSf membrane as a feed pressure functions at 35°C.

of CO₂ at 2 bar is approximately 205 K (- 68°C), while at 5 bar, it is approximately 218 K (- 55°C). Thus, in the temperature range evaluated in this study, there is no possibility of CO₂ condensation in the polymeric matrix. The gas-polymer interaction is significant for the Henry's mode, while gas condensability and the free volume in the polymer are significant to the Langmuir mode. At low pressures, the Langmuir mode has a higher influence on the solubility coefficient than Henry mode. Regarding the impossibility of condensation of CO₂ in the polymer matrix, the influence of free volume is the determining factor considered in the analysis of solubility coefficient.

Robeson et al. (2014) presented the Equation 9 to determine the diffusivity coefficient in steady state (D_{sec}). Such equation is obtained from Equations 5 and 6, considering the Dual-mode model.

$$D_{sec} = \frac{P}{S_{sec}} = \frac{K_D \cdot D_D \cdot (1 + (F \cdot K / (1 + bP_2)))}{K_D + (C'_H \cdot b / (1 + bP_2))} \quad (9)$$

Where: S_{sec} is the solubility coefficient in steady state.

Figure 7 shows the predicted values of diffusivity coefficient from Equations 8 and 9. The Dual-mode model constants applied in Equation 9

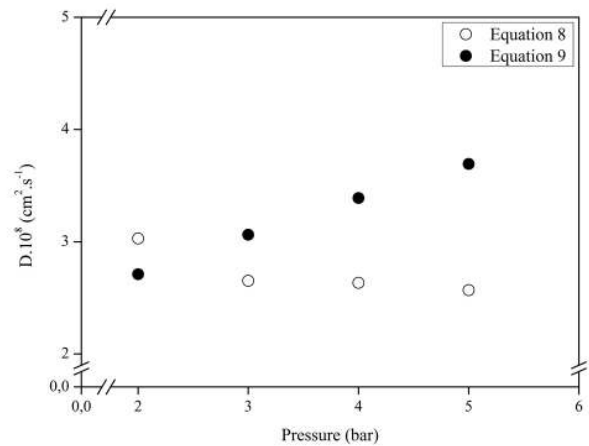


Figure 7 - Diffusivity coefficients predicted by Equations 7 and 8.

were obtained by Hu et al. 2003 for chloroform at 35°C.

The diffusivity coefficients showed a typical behavior for the permeation of non-condensable gases in non-porous polymeric membrane (Basile and Nunes 2011). According to the Table I, $C'_H \cdot b$ is higher K_D , which means that the Langmuir sorption is more important than the Henry sorption in Dual-mode model. Langmuir mode is more sensitive to pressure than the Henry mode. Therefore, diffusivity behavior according to the Equation 9 is in agreement with the predicted by the Dual-mode model. Equation 8 is an experimental data fit, and the diffusivity behavior is associated with permeability (P), i.e., diffusivity has the same behavior of the permeability measured from Equation 1.

Figures 8 and 9 present the behavior of the solubility and diffusivity coefficients in function of temperature.

Regarding to temperature influence on solubility coefficient, with its increase, there is a reduction in the permanent free volume (microvoids present in the dense layer, related to the Langmuir mode) due to the thermal rearrangement of the polymer chains, thus reducing the solubility coefficient of the Langmuir mode. Similar results were found by Wang and Kamiya (1995). At same time, increasing temperature, there

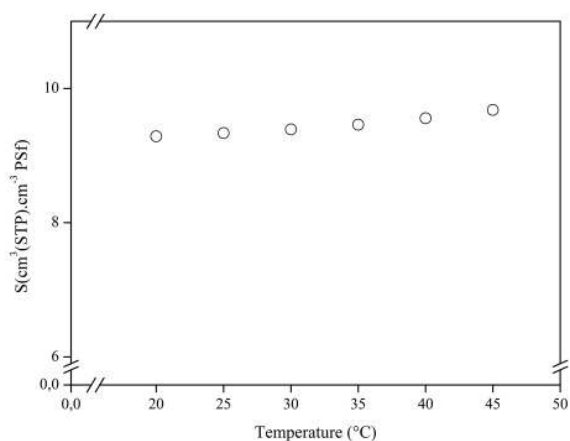


Figure 8 - CO₂ solubility coefficients in PSf membrane as a temperature function at 2 bar.

is an increase in the solubility coefficient related to Henry's mode, due to the higher activation energy of permeation responsible for increase transient voids (intersegmental spaces), resulting in higher sorption by the Henry's mode. In fact, within the temperature range studied the modes are practically compensated, with no significant influence on the solubility. However, the diffusion coefficient increases with increasing operating temperature, according Magnanelli et al. (2016), this is because the membrane not be supported. The increase in temperature increases the vibrational energy in the polymeric chains, therefore increases the activation energy of permeation for the molecules perform the diffusive jumps within the transient spaces by Langmuir mode (sorbed molecules in the permanent free volume of the polymeric matrix) and through Henry's mode (sorbed molecules in the intersegmental spaces in the polymeric chains).

CONCLUSIONS

The CO₂ permeability through membrane ranged since 18.8 Barrer at 2 pressure until 15.4 Barrer at 5 bar pressure (35°C), presenting a smooth reduction in permeability with increasing pressure, especially above 3 bar pressure. It was not observed CH₄ permeability for 2 and 3 bar pressure (35°C), while

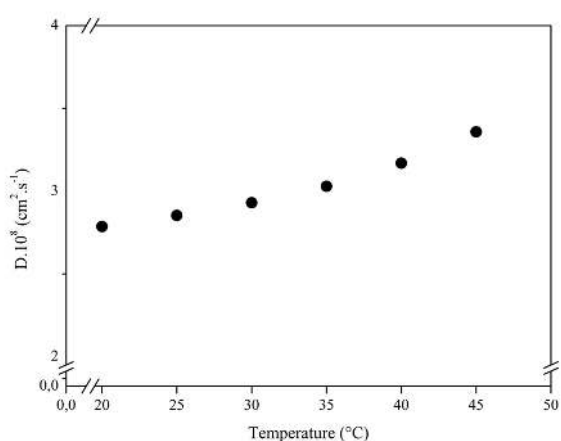


Figure 9 - CO₂ diffusivity coefficients in PSf membrane as a temperature function at 2 bar.

between 3 and 4 bar there was a little increased in your permeability (from 3.1 to 3.3 Barrer). The CO₂ permeability's behavior was similar to that predicted by the Dual-mode model, although the permeability predicted by model has been lower than the experimental values.

The activation energy of CO₂ permeation in the membrane decreases with increased pressure, i.e., permeability increases with increasing temperature for all pressures evaluated.

The absence of methane permeability at 2 and 3 bar pressure, qualifies the membrane for the separation of gases with high selectivity in this range.

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