Ultem®/ZIF-8 Mixed Matrix Membranes for Gas Separation: Transport and Physical Properties

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Mixed matrix membranes are promising options for improving gas separation processes. Zeolitic imidazolate frameworks (ZIFs) have a porous structure similar to conventional zeolites, being capable in principle of separating gases based on their differences in kinetic diameter while offering the advantage of having a partial organic character. This partial organic nature improves the compatibility between the sieve and the polymer, and a combination of the mentioned characteristics makes these hybrid materials interesting for the preparation of mixed matrix gas separation membranes. In this context the present work reports the preparation of Ultem®/ZIF-8 mixed matrix membranes and their permeabilities to pure CO_2, N_2 and CH_4 gases. A significant increase in permeability with increase in CO_2/N_2 selectivity was observed for the mixed matrix systems as compared to the properties of the neat Ultem®. Sorption results allowed to speculate that the ZIF-8 framework is not completely stable dimensionally, what influences the separation process by allowing gases with higher kinetic diameter than its nominal aperture to be sorbed and to diffuse through the crystal. Sorption and diffusion selectivities indicate that the higher separation performance of the mixed matrix membranes is governed by the diffusion process associated with the influence of gas molecule´s geometry.

Keywords: *ZIF-8, mixed matrix membranes, Gas separation, Gas permeation, Gas sorption*

1. INTRODUCTION

Mixed matrix membranes are promising alternative for the development of gas separation new materials membranes. Mixing polymeric materials with zeolites or other types of molecular sieving media creates membranes with properties that overcome the properties of the polymeric matrix. Such hybrid materials can also offer the advantage of low cost and better mechanical properties of the polymer when compared to typical inorganic membranes[1-3].

Successful defect-free mixed matrix membrane preparation has been reported especially when the polymer matrix is a rubbery polymer, since the flexible matrix promotes the formation of defect-free polymer/sieve interface[4]. For glassy polymers the formation of defect-free membranes can be achieved by the compatibilization of the two phases with silanes as reported in the literature[3,5]. Unfortunately, high performance membranes are more complex to obtain, due to difficulties in avoiding the formation of interfacial defects between the dispersed and continuous matrix phases[6-10].

Zeolitic imidazolate frameworks (ZIFs)[11-13] created a new possibility for mixed matrix membranes formation. The partial organic character of ZIFs, as a consequence of the imidazolate links, makes them more compatible with organic polymer matrices used for the preparation of mixed matrix membranes. The intrinsically more compatible nature of polymer/ZIF hybrids promote the achievement of defect

free membranes without the need of high temperatures membrane processing or complex compatibilization protocols.

ZIFs are a subclass of metal organic frameworks (MOFs) that have being considered promising for applications as gas storage and gas separation materials. The structure of ZIFs comprises chemical complexes of transition metals like zinc and cobalt with imidazolates[11]. The angle between the imidazolate links and the metal cluster is similar to the angle in conventional zeolite bonds, thereby making it possible to create ZIFs with structures similar to inorganic zeolites[12]. When compared to inorganic zeolites ZIFs have a high sorption capacity as a consequence of their higher surface areas and pore volumes[13]. Moreover the ZIFs still possess pores windows connected through small apertures. In ZIF-8 the pores have diameter of 11.6 Å with an aperture of 3.4 Å. Other characteristics of the ZIFs include low density, high thermal and chemical stability, periodicity and systematic variation of pore size and porosity[14–16]. In terms of gas separation ZIF-8 has been studied in a great number of applications due to its aperture size that lies in the size range of the kinetic diameter of various gases including CO_2, CH_4 and N_2. Also ZIFs and their mixed matrix membranes are considered as promising alternatives for the development of efficient and economically affordable capture technologies under both post-combustion and pre-combustion conditions[17,18]. Their potencial lies in the great number of chemical compositions and particle morphologies that can be achieved during the synthesis of ZIFs[18] and it is because

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of that potencial that they have received a lot of attention of academy and industry.

Several studies have reported the adsorption of different gases in ZIFs membranes and other MOFs, including molecular simulations and some experimental data[19–21]. Nevertheless, fewer works have considered application of these materials in mixed matrix membranes[22–25]. Recent work from Zhang and co-workers showed an improvement on propylene/propane permeation and selectivity of 6FDA-DAM polyimide membranes with the incorporation of ZIF-8 particles for propylene/propane[23]. Dai and co-workers reported the development of Ultem®/ZIF-8 hollow fiber mixed matrix membranes with higher selectivity than the neat Ultem® membrane for CO_2/N_2[26].

After that a series of works have been published in the area of mixed matrix membranes based on ZIFs[27-31] including the formation of hollow fiber mixed matrix membranes and based on ZIF-8 for propylene/propane separation[28] and Mixed-linker zeolitic imidazolate framework mixed-matrix membranes for aggressive CO_2 separation from natural gas[29].

In this work preparation of Ultem®/ZIF-8 mixed matrix membranes and their permeabilities to CO_2, N_2 and CH_4 and their CO_2/CH_4, CO_2/N_2 ideal selectivities are reported. Separation of carbon dioxide and methane is considered in this paper due to its importance in natural gas processing while CO_2/N_2 separation has great importance for the treatment of flue gas from post combustion process. Aside from the possible applications of the membranes this work intended to get more information on the sorption process of the three gases in ZIF-8 which gives more evidences to support the idea of the flexibility of ZIF-8 framework. It is also evidenced that although the incorporation of ZIF-8 has a positive effect in terms of the diffusion selectivity it decreases the solubility selectivity of the final membranes when compared to the polymer. The results also gives strong evidence of the importance of entropic effects related to the geometry of gas molecules on the separation properties of Ultem®/ZIF-8 mixed matrix membranes. The final conclusion is that the incorporation of ZIF-8 increases CO_2 permeability without sacrificing CO_2/CH_4 and CO_2/N_2 selectivities.

2. Materials and Methods

2.1. Materials

ZIF-8 particles with the trade name Basolite Z1200, bulk density of 0,35 g/cm³ and mean particle size 4.9 μm (D50) were purchased from Sigma-Aldrich – USA and Ultem® 1000 with bulk density of 1.27 g/cm³ and Tg of 217 °C was purchased from Sabic Innovative Plastics – USA. Methylene chloride was used as solvent for Ultem®. All gases used in permeation and sorption tests have purity of 99.999% and were obtained from local Air Liquide or Air Products.

2.2. Membrane Preparation

Before membrane formation, the ZIF-8 particles were heated at 200 °C in a vacuum oven over night for activation and then kept in a convection oven at 100 °C. The polymer was heated at 100 °C in a convection oven over night.

ZIF-8 was dispersed in methylene chloride for 10 minutes by using a tip ultra-sound processor which led to the formation of a milk-like suspension. Afterwards the polymer Ultem® was added to the milk-like suspension to form a suspension of ZIF-8 in a solution of Ultem® in methylene chloride. Membranes with 10wt% and 30wt% of ZIF-8 in Ultem were prepared and named UZ10 and UZ30, respectively. The compositions were obtained by carefully weighting the mass of each component during the preparation of polymer-sieve dispersions. Membranes were prepared by casting the suspension prepared onto a glass plate. The cast films were kept inside a glove bag purged with nitrogen and saturated with methylene chloride for a period of 24 hours, after which they were peeled off from the glass plate and dried in vacuum oven to remove the solvent excess.

The drying protocol was conducted from room temperature to 100 °C. The temperature was slowly increased and then kept at 100 °C for 5 days to assure that all solvent was removed.

The thickness of the membranes varied between 63 and 92μm as evidenced by SEM images in Figures 4a-c.

2.3. Maxwell Model

The model proposed by Maxwell for predicting properties of dielectric blends has also been widely used to describe the transport properties of mixed matrix membranes composed of moderate loadings of spherical particles (Eq.1)[32].

$$P_{MMM} = P_C \left[\frac{P_d + 2P_C - 2\phi_d (P_C - P_d)}{P_d + 2P_C + \phi_d (P_C - P_d)} \right] \quad (1)$$

Where P_{MMM} is the permeability in the mixed matrix membrane, P_d is the permeability in the dispersed phase, is the volume fraction of the dispersed phase and P_C is the permeability in the unmodified continuous phase.

Although the model describes ideal transport properties of mixed matrix membranes, it has limitations when non-ideal effects exist like sieve-in-cage, matrix rigidification and stress dilated matrices[7,10]. To account for non-ideal effects one can apply a "nested" version of the Maxwell model. This approach relies upon calculating the permeability of a pseudophase (P_{eff}) composed of the sieve and the matrix around it and then using this value to calculate the permeability of the three phase membrane (P_{3MMM}). Equations 2 and 3 describe the two models used[10].

$$P_{eff} = P_I \left[\frac{P_d + 2P_I - 2\phi_d (P_I - P_d)}{P_d + 2P_I + \phi_d (P_I - P_d)} \right] \quad (2)$$

$$P_{3MMM} = P_M \left[\frac{P_{eff} + 2P_C - 2(\phi_d - \phi_I)(P_C - P_{eff})}{P_{eff} + 2P_c + (\phi_d - \phi_I)(P_C - P_{eff})} \right] \quad (3)$$

Where P_I is the permeability of the polymer around the particle, ϕ_S is the volume fraction of the particle in the pseudophase and ϕ_I is the volume fraction of the interphase in the membrane.

The permeability of the interphase equals the permeability of the polymer divided by a factor β, which is assumed to have values between 0 and 1 for stress dilated matrix--and is larger than 1 for matrix rigidification.

By applying such a Maxwell model, one can estimate the permeability of a zeolite if the permeability of mixed matrix membranes can be described.

2.4. Characterization

The glass transition temperature of the membranes was determined with differential scanning calorimetry. The tests were performed in a TA equipment (DSC-Q2000) by heating the samples from 40 °C to 250 °C, keeping this temperature for 3 minutes and then cooling to 35 °C at a rate of 45 °C/minute and heating again to 250 °C. The heating rates were 10 °C/min. ZIF-8 and the mixed matrix membranes were characterized by SEM in field emission electron microscope PhillipsXL30. Mixed matrix membranes were fractured with liquid nitrogen and sputter coated with gold before analyses.

Wide Angle X-Ray Diffraction was performed to verify the crystalline structure of ZIF-8. The tests were conducted in a Rigaku Geiger-Flex equipment using Cu K α radiation.

Pure gas permeation measurements were performed at 35 °C and 100 psi for CO_2, N_2 and CH_4 gases following procedures described in details elsewhere[33,34]. A so-called pressure decay sorption technique was conducted to determine the sorption capacity of ZIF-8 and of the membranes following procedure described in details elsewhere[35].

3. RESULTS

3.1. Characterization of ZIF-8

Figure 1 shows WAXD results for ZIF-8 and the most important planes corresponding to the sodalite structure of ZIF-8 (card crystallographic number: 7111968).[36,37] The peak that appears at $2\theta=7,46^{\circ}$ represents the plane (011) of ZIF-8 crystalline structure and is usually used as reference for the identification of ZIF-8. Figure 2 shows the morphology of the ZIF-8 particles used in this work. The morphology shows that the shape and size of the particles are relatively homogeneous although it is possible to observe some bigger particles.

Figure 3 shows the sorption isotherms of nitrogen, methane and carbon dioxide in ZIF-8 at 35 °C fitted to the Langmuir model. It is clear that ZIF-8 has a higher than expected sorption capacity for N_2 and CH_4 considering its nominal aperture size (3.4 Å). Taking into account the kinetic diameters of nitrogen (3,64 Å) and methane (3,8 Å) it would be expected that ZIF-8 particles would reject the gas molecules which would lead to a much lower sorption capacity for the two gases as observed for conventional zeolites. The separation mechanism involved is called molecular sieving effect[38]. Since ZIF-8 particles are not able to avoid the gas molecules from accessing its porosity the overall separation capacity of the mixed matrix membranes will be affected in a negative fashion. A direct consequence of the high sorption capacity and relatively high diffusion coefficients of these gases in the ZIF-8 crystal is that the permeability of both nitrogen and methane increase with the addition of ZIF-8, which may be considered a direct consequence of its high sorption capacity and relatively high diffusion coefficients of these gases in the ZIF-8 crystal.

A possible explanation for the observed results could be the reported flexibility of the imidazolate links presented in the structure of ZIFs. Using experimental and mathematical simulation data it was suggested that the structure of ZIFs and MOFs may be somewhat flexible, which could increase
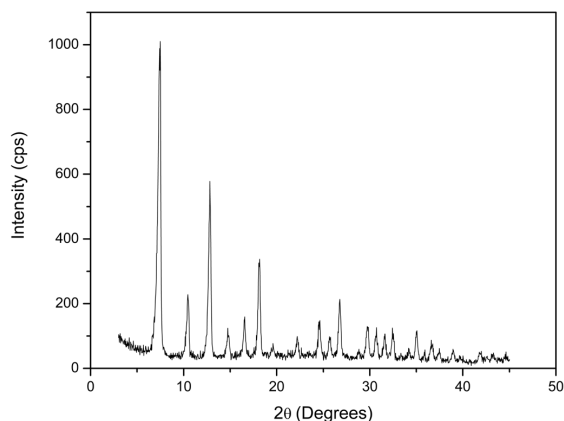

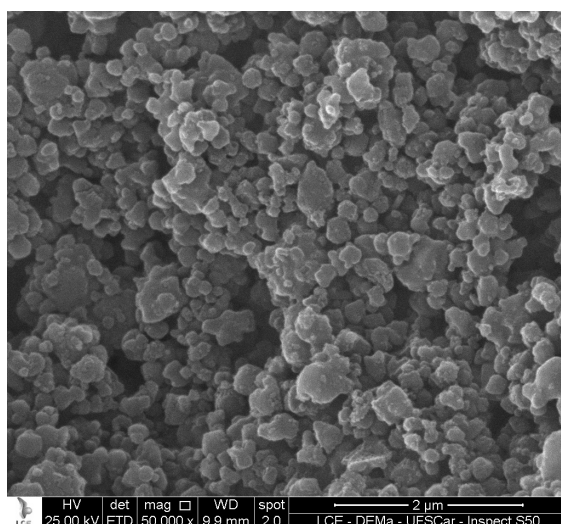**Figure 1**: XDR difratograms of ZIF-8.

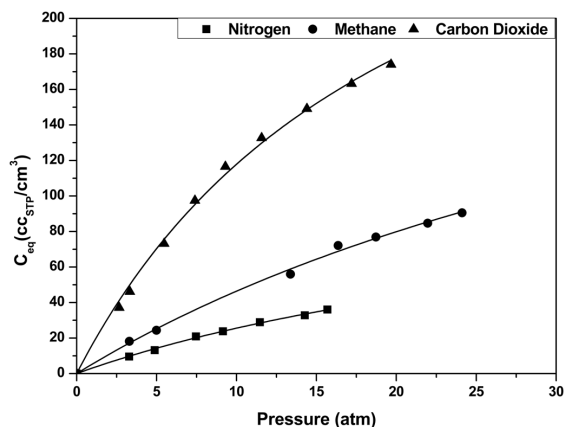**Figure 2**: SEM images of ZIF-8 particles.

Figure 3: Sorption isotherms of ZIF-8 (35oC).

the effective size of their aperture in comparison to the 3.4 Å reported size based on modeling of a rigid ZIF-8 crystal[39-41]. The idea of the flexibility of ZIF-8 framework has been used to explain CH_4 and N_2 adsorption data in ZIF-8[42,43]. The actual characterization of ZIF-8 flexibility is complex and is not considered in details in this work. In any case, the fact that the sorption tests shows high sorption capacity of ZIF-8 for gases molecules larger than its nominal aperture is a strong indicative of its possible flexible behavior.

3.2. Thermal and Morphological Characterization of the Mixed Matrix Membranes

Figure 4 presents SEM images of Ultem® and Ultem®/ZIF-8 mixed matrix membranes. Figures 4d-f show that in this range of magnification there are no large agglomerates or defects that could be detrimental to the properties of the mixed matrix membranes. Figure 4g shows a larger magnification of the
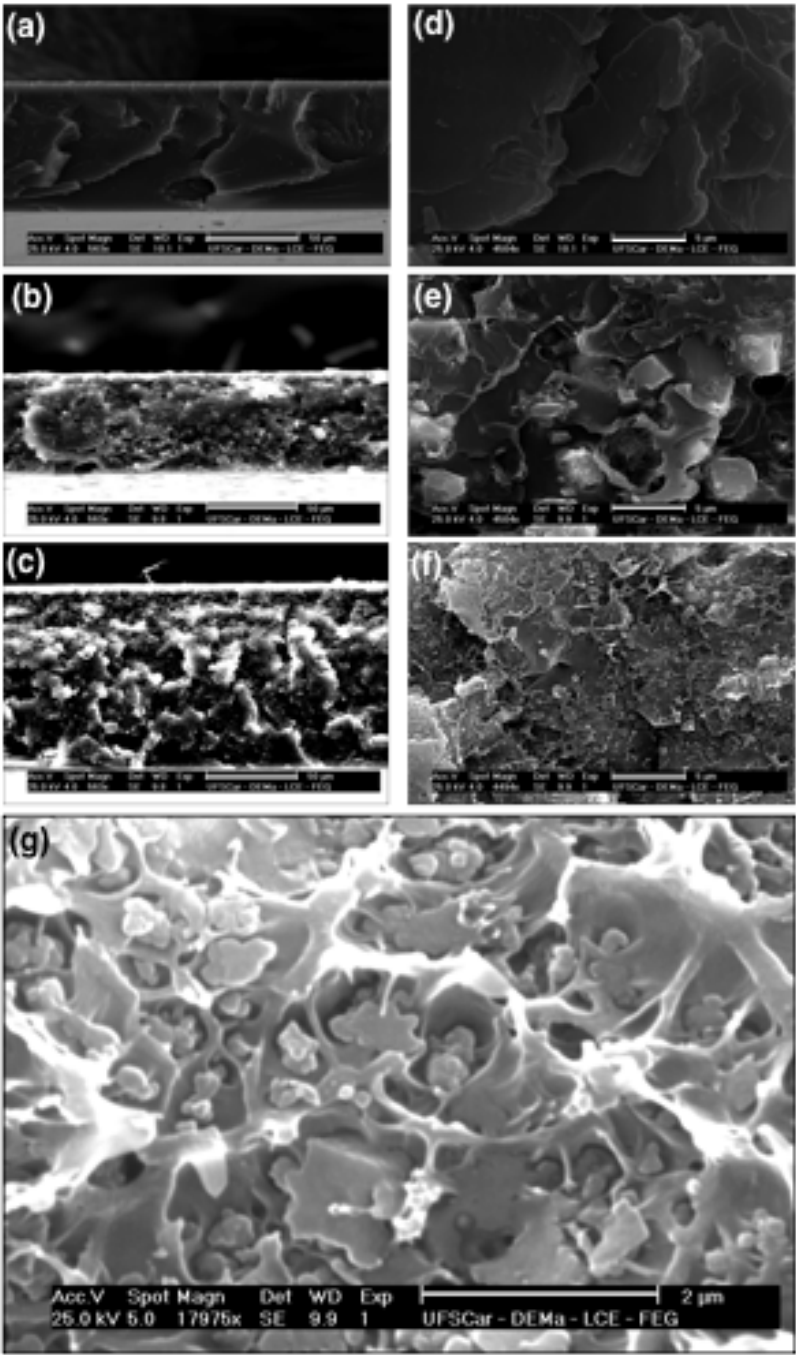

Figure 4: SEM images of Ultem®/ZIF-8 mixed matrix membranes. (a) and (d) Ultem®, (b) and (e) UZ10, (c), (f) and (g) UZ30.

morphology of sample UZ30. The morphology is similar to the morphology of ZIF-8 mixed matrix membranes presented by other researchers[23]. According to that there is a tendency of agglomeration of ZIF-8 particles at high particle contents[23]. It has also been suggested that the concentric cavities observed around ZIF-8 particles are a evidence of the strong interfacial contact between the particles and the polymer although they could be the result of cryogenic fracturing during sample preparation[23]. In general the morphology observed in Figure 4g is expected for mixed matrix membranes prepared by solution casting of polymer/sieve dopes that are obtained from dried particles. Alternative membrane preparation techniques that uses emulsion techniques give different morphologies with better adhesion[44] but in terms of regular solution casting adhesion and dispersion presented in Figure 4 is considered good for the production of good membranes.

DSC analyses were conducted to determine the T_g of the mixed matrix membranes and of the neat polymer. Such data is important because the temperature used for solvent removal after membrane formation was considerably lower than the T_g of the polymer Ultem®. To compensate for the low temperature used in the drying process of the membranes the annealing time was increased to ensure complete solvent removal. An indication that this procedure was successful is provided by the properties of the matrix Ultem® in the pure and mixed matrix samples prepared in this work, which are consistent with literature data. The T_g of the mixed matrix membranes are reported in Table 1. The results obtained for the first heating (T_{g1}) indicates that the solvent was removed from the membranes after the long annealing protocol. The T_g of the membranes is just slightly lower than the reported value for Ultem® in the literature[32], which may be a result of the relatively low temperatures used to anneal the samples. The second heating (T_{g2}) indicates that any processing and thermal history that would influence the properties of the membranes were erased by heating the material at temperatures higher than the T_g. It is also possible to note some influence of ZIF-8 particles on the T_g of the polymer specially with 30 wt% loading (UZ30). The most important observation from these results is the absence of indicative of sieve-in-cage morphology, which might make the T_g of mixed matrix membranes to be smaller than the T_g of the polymer[45,46]. This result agrees with the observations in SEM images and confirms that one of the objectives of

the work was achieved that is the formation of defect-free membranes without the use of high temperature protocols or compatibilization.

In terms of the removal of adsorbed solvent from ZIF-8 the low temperature should not be a problem considered the hydrophobic nature of ZIF-8[47]. It has been shown that ZIF-8 has a intrinsically hydrophobic nature that results from the methyl group of the imidazolate link and also from the fact that the most favorable sites for adsorption are not accessible in ZIF-8 as in other ZIFs that are considered hydrophilic[47,48]. As a consequence of its hydrophobicity ZIF-8 presents an extremely low water uptake and also a low uptake for short chain alcohols like ethanol that are more polar. Considering that the dipole moments of ethanol and methylene chloride are close it is expected that ZIF-8 will not adsorb much of the solvent and the low temperatures used to treat the membranes will not affect the final membrane performance. This is also evidenced by the high sorption uptake of the mixed matrix membranes when compared to the polymer which shows that the pores of ZIF-8 are accessible for the gases.

3.3. Pure gas permeation and sorption

Pure CO_2, N_2 and CH_4 permeation measurements were performed for neat Ultem® and Ultem®/ZIF-8 membranes. Table 2 summarizes the permeabilities and ideal selectivities of Ultem® and the mixed matrix membrane containing 30 wt% of ZIF-8 (UZ30). The permeability of the polymer Ultem® is in accordance with data reported previously[49], which indicate that with the drying conditions used in this work essentially all residual solvent was removed. The selectivity of the polymer for both gas pairs also agrees with values reported in the literature. The importance of this simple observation lies on the fact that the temperatures used to heat the membranes were well below the Tg of the polymer.. For some reason, which we still do not yet understand, heating the membranes above 100 °C tended to cause formation of defective membranes; however, the lower temperature combined with the long time evacuation avoided this problem.

The permeability for the three gases tested increased with the incorporation of ZIF-8 in Ultem®. CO_2 permeability increased from 1.54 Barrer to 3.25 Barrer and to 11.1 Barrer with the incorporation of 10 (UZ10) and 30 (UZ30) wt% of ZIF-8, respectively. These values represent an increase of approximately 110% and 620% for each one of the compositions. Nitrogen permeability increased from 0.058 Barrer to 0.095 Barrer and 0.357 Barrer with incorporation of 10 and 30 wt% of ZIF-8. Methane permeability follows the same trend increasing from 0.041 Barrer to 0.083 Barrer and to 0.274 Barrer in the mixed matrix membranes containing 10 and 30 wt% of ZIF-8 respectively. The percentage of increase for N_2 and CH_4 were 65% (10 wt%) and 516% (30 wt%) and 105% (10 wt%) and 580% (30 wt%) respectively.

Table 1: Glass transition temperatures of pure Ultem® and the mixed matrix membranes obtained from DSC analyzes.

Sample	Tg$_1$ (ºC)	Tg$_2$ (ºC)
Ultem®	206	215
UZ10	206	216
UZ30	215	219

Table 2: Permeability and ideal selectivity of Ultem® and the mixed matrix membranes.

Material	Permeability (Barrer)			Ideal Selectivity	
	CO$_2$	N$_2$	CH$_4$	CO$_2$/CH$_4$	CO$_2$/N$_2$
Ultem®	1.535	0.0579	0.0405	37.9	26.52
Ultem®/ZIF-8 (UZ30)	11.1	0.357	0.274	40.4	31.11

The results observed in permeation tests can be partially explained by the high sorption capacity of ZIF-8 for all three gases. The permeability for the mixed matrix membranes follows the sequence $CH_4 < N_2 < CO_2$.

Figure 5 shows the sorption isotherm at 35°C for Ultem® and the mixed matrix membrane containing 30 wt% of ZIF-8 (UZ30). For each gas it is clear that the sorption capacity of the mixed matrix membrane is higher than that of the neat polymer. Table 3 summarizes Henry's Law and Langmuir sorption coefficients obtained by fitting the data to the dual mode sorption model[33]. From the data obtained the sorption selectivity was calculated for the neat polymer and for the mixed matrix membrane UZ30 at 100 psi.

3.4. Diffusion of CO_2, CH_4 and N_2 in the mixed matrix membranes

Diffusion coefficients for each gas were calculated based on permeation and sorption data, since D=P/S, based on the sorption-diffusion transport model in membranes. Table 4 summarizes the results obtained.

The diffusion coefficients follow the sequence $CH_4 < N_2 < CO_2$ for both Ultem® and the mixed matrix membrane UZ30 which correlates with the kinetic diameter of the gas molecules. The diffusion selectivity increases for both gas pairs studied with the incorporation of ZIF-8, but the increase is more evident for CO_2/N_2 than for CO_2/CH_4 which indicates
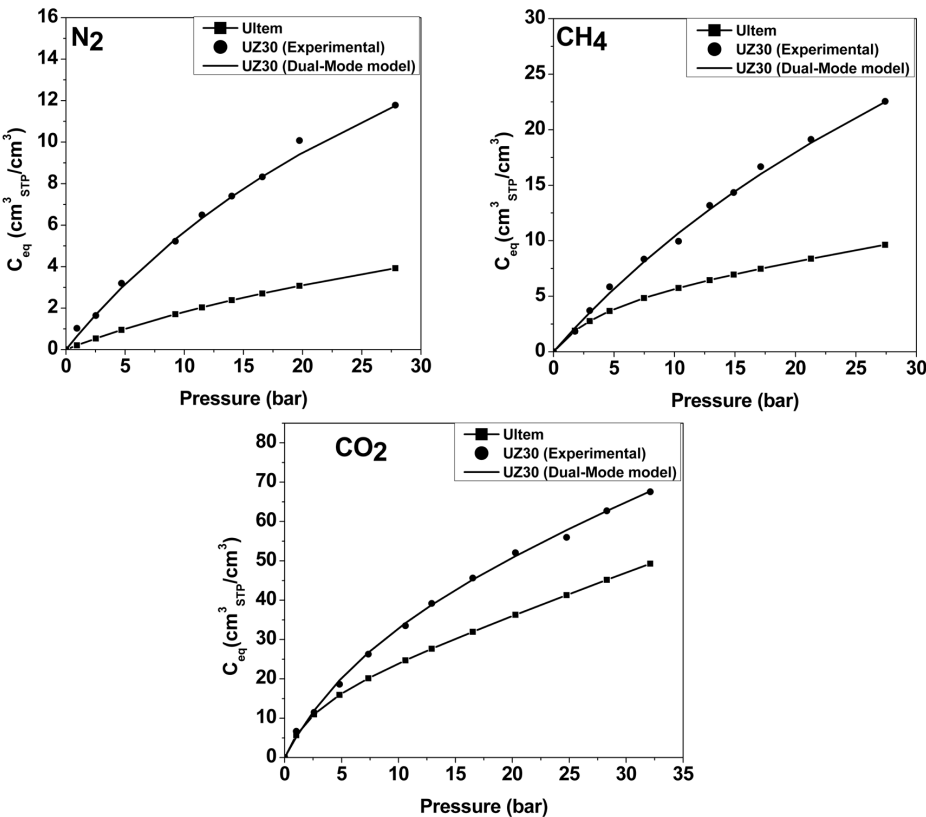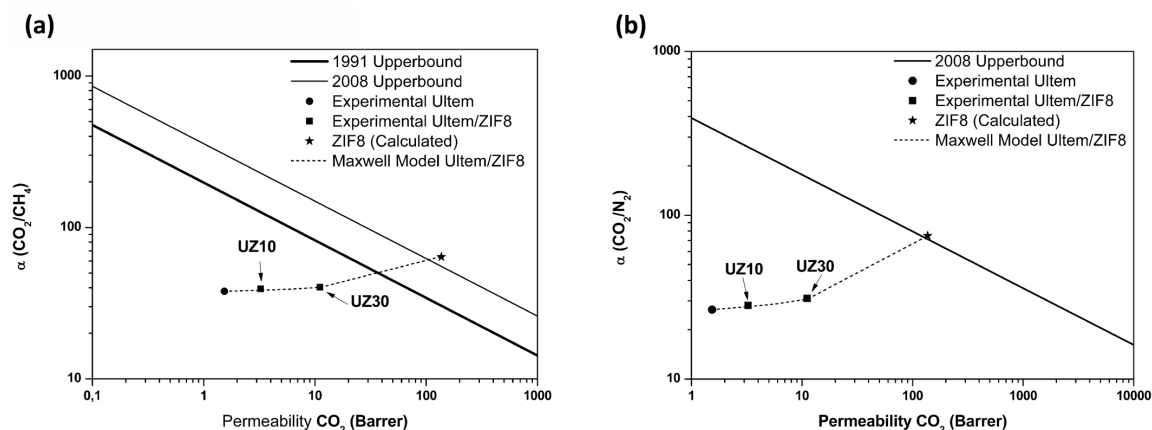

Figure 5: Sorption isotherms of the mixed matrix membranes fitted to the Dual-Mode Model (35oC).

Table 3: Henry and Lagmuir coefficients obtained from the sorption data for Ultem® and the mixed matrix membranes containing 30wt% of ZIF-8.

Material	S ($cc_{STP}/cm^3 \cdot atm$)			S_i/S_j	
	CO_2	N_2	CH_4	CO_2/CH_4	CO_2/N_2
Ultem®	2.84	0.193	0.674	4.2	14.7
Ultem®/ZIF-8 (UZ30)	3.79	0.627	1.21	3.12	6.0
ZIF-8	13.34	2.71	4.87	2.73	5.0

Table 4: Diffusion Coefficients and diffusion solubility for Ultem® and UZ30.

Material	D (cm^2/s)			D_i/D_j	
	CO_2	N_2	CH_4	CO_2/CH_4	CO_2/N_2
Ultem®	4.11×10^{-09}	2.27×10^{-09}	4.57×10^{-10}	9.0	1.8
Ultem®/ZIF-8 (UZ30	2.33×10^{-08}	4.48×10^{-09}	1.97×10^{-09}	11.8	5.2

Figure 6: Ideal Selectivity of Ultem® and the mixed matrix membranes. (a) CO2/CH4 and (b) CO2/N2.

that nitrogen diffusion coefficient is less affected by the incorporation of ZIF-8 than methane diffusion coefficient. This observation could be explained by entropic effects related to the geometry of each molecule as discussed by Koros and co-workers[50]. Entropic effects lead to high separation performance in molecular sieves due to their ability of restricting the motion of molecules like nitrogen in the transition state. The restriction is a consequence of the loss of the rotation of nitrogen molecules due to their geometry. That way nitrogen geometry would restrain its diffusion inside ZIF-8 pores.

3.5. Separation Performance of the mixed matrix membranes

The incorporation of ZIF-8 has little effect in the selectivity of Ultem® for both gas pairs. CO_2/N_2 ideal selectivity increased from 26.5 to 31.1 for the membrane containing 30 wt% of ZIF-8 as compared to the neat polymer membrane which represents an increase of 14.7%. The results are in accordance with data from Dai and co-workers for Ultem®/ZIF-8 hollow fiber membranes where it was obtained a 20% increase in CO_2/N_2 ideal selectivity[26] considering the differences in the processing of flat and hollow fiber membranes that result in the orientation of polymer chains in the fibers and higher selectivity. CO_2/CH_4 ideal selectivity was increased by 6.5% with the incorporation of the same amount of ZIF-8. In summary the results indicate that the incorporation of ZIF-8 led to an increase in CO_2 permeability without sacrificing the selectivities of each gas pair.

Considering the solubility selectivities and the diffusivity selectivities and their effects on the overall ideal selectivity it can be rationalized that ZIF-8 has a detrimental effect on sorption selectivity for both gas pairs. In the case of Ultem® this effect is more relevant for CO_2/N_2 due to the high sorption selectivity of the polymer for this gas pair. On the other hand in terms of diffusion selectivity ZIF-8 has positive effects for both gas pairs and again the effect is more pronounced for CO_2/N_2 in the case of Ultem®. Based on these observations it could be stated that the contribution of ZIF-8 for the separation performance of the mixed matrix membranes lies strongly on the diffusion process. Moreover it seems that the geometry of the gas molecules and its

contribution to the diffusion process has more influence in the separation performance of the mixed matrix membranes than the kinetic diameter of each molecule which is evidenced by the increase in diffusion selectivity of CO_2/N_2 compared to the diffusion selectivity for CO_2/CH_4.

Figure 6 shows the CO_2/CH_4 and CO_2/N_2 ideal selectivity for Ultem® and the mixed matrix membranes plotted versus CO_2 permeability. The experimental data is compared to the upper bound line[51,52], showing that the incorporation of ZIF-8 does not contribute to the improvement of the selectivity of the membranes towards the upper bound line but it strongly affects the permeability without sacrificing the selectivity of the polymer.

4. CONCLUSIONS

Ultem®/ZIF-8 mixed matrix membranes were prepared by solution casting, which created defect free membranes with overall good ZIF-8 dispersion. Great increases on the permeability of the polymer were observed with the incorporation of the ZIF-8. The selectivity of the mixed matrix membranes was not sacrificed by the incorporation of ZIF-8. Strong evidence of ZIF-8 flexibility was obtained from sorption experiments that indicated the great sorption capacity of ZIF-8 for N_2 and CH_4. Diffusion selectivity for CO_2 vs. N_2 and CH_4 of the mixed matrix membranes was higher than the neat polymer. The increase in diffusion selectivity was the key determinant for the increase in overall ideal selectivity. Based on sorption data for ZIF-8 and diffusion selectivity for the mixed matrix membranes it can be concluded that the separation process of Ultem®/ZIF-8 mixed matrix membranes is influenced by the geometry and critical temperatures of the various gas molecules; however, size-dependent diffusion effect played the most important role on the ideal selectivity of the mixed matrix membranes.

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