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THERMODYNAMIC EVALUATION OF CO_2/CH_4 TRANSPORT BEHAVIOR OF POLYBLEND FILMS

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Resumo – A solubilidade e a difusividade de CO_2 e CH_4 através de vários sistemas poliméricos têm sido objeto de vários estudos. O obejtivo deste trabalho é a obtenção de membranas poliméricas capazes de conferir alta permeabilidade e alta seletividade para o sistema dióxido de carbono/metano, o que é de particular interesse da indústria de exploração petrolífera. Membranas obtidas a partir da mistura de poli(metacrilato de metila) e poli(fluoreto de vinilideno), (PMMA/PVDF), modificadas superficialmente através de hidrólise ácida, foram avaliadas por FTIR, com respeito à sua utilização como membranas de separação de gases. Essa avaliação foi feita permeando a mistura CO_2/CH_4 através das membranas preparadas, utilizando célula de gas especial.
Os coeficientes de difusividade, a permeabilidade e solubilidade foram calculados para as membranas poliméricas, possuindo diferentes espessuras, mostrando o efeito desta variável no transporte da mistura de gases. Os dados foram analisados com base na teoria bimodal, considerando a contribuição global da difusão dos gases através das membranas, que responde pelo fator cinético do processo de permeação e da solubilização das moléculas de gas na matriz polimérica, definida por interações do tipo ligação de hidrogênio, forças de Van derWaals, etc. Os fatores cinéticos, caracterizados pelo coeficiente de difusão, D, e as condições termodinâmicas, expressas pelo coeficiente de solubilidade, S, são determinados pela estrutura e morfologia do polímero e pela natureza dos gases permeantes envolvidos no sistema.

Palavras-Chave: membranas; permeabilidade; misturas de gases

Abstract – Poly(methyl methacrylate)/poly(vinylidene fluoride) (PMMA/PVDF) blends, surface modified by hydrolysis, were evaluated regarding their use as improved gas separation membranes able to provide high permeabilities and high separation factors for carbon dioxide/methane gas mixtures, which is of great interest for the petroleum recovery industry This was done using a FTIR spectroscopy technique with a special gas cell to measure the permeation, diffusion and solution coefficients of carbon dioxide and methane gases, both pure and as a 50:50 mixture, through the membranes. Those transport properties were determined as functions of temperature, film thickness and degree of surface hydrolysis.

It was found that surface hydrolysis of part of the PMMA blend component, by H_2SO_4 solution, to poly(methacrylic acid) caused an increase in CO_2 permeation with lesser change in CH_4 permeation. This gave both an increase in the separation of the gas mixture and an increase in the yield flux of CO_2. It also was found that the separation efficiency was greater for the thicker membrane (17μm) than for the thinner membrane (8 μm), for nominally the same degree of surface region hydrolysis.

The differences in transport coefficients and their thermodynamic parameters between pure gases and gases in the mixture indicate that there is sorption/diffusion site competition between the CO_2 and CH_4 molecules within the membrane. The CO_2 apparently is preferentially sorbed, leading to an enhanced rate of CO_2 transport and increase in the separation factor, α. There also seems to be a selectivity enhancement for CO_2 in the concurrent diffusion process. That aspect is not as well defined.

Keywords: membranes; permeability; gas mixtures

1. Introduction

Although the idea of gas separations by membrane permeation can be found in publications from the last century, it was only recently that separation of gases by such techniques reached full-scale commercial practice. A major advance in this field was the introduction of hollow fiber membrane technology by Monsanto, based on polysulfone, which found initial applications in hydrogen recovery. Since then, several more membrane systems based on other polymers have become commercially available and are being used for a variety of separations. In spite of this recent progress, there still is considerable interest in new membrane materials that will provide further improvements in performance characteristics for specific applications. While many factors determine the success of a membrane, an advantageous combination of productivity and selectivity is an especially desirable one[1].

For a membrane to present good separation efficiency, it must have ~~a~~ high permeability for a specific component to be separated from the mixture, high selectivity for that component, good mechanical, thermal and chemical resistance properties and it must be free of pinholes and other defects to assure homogeneity. The balance between the first two requirements is the main challenge in the preparation of efficient membranes, for high permeability almost always means low selectivity.

Polyblend films composed of poly(methyl methacrylate)(PMMA) and poly(vinylidene fluoride)(PVDF) have been made with the purpose of developing high efficiency gas permeation membranes presenting also good mechanical properties. The main objective of this study is to obtain both high permeabilities and high separation factors for carbon dioxide/methane gas mixtures, which is of great interest for the petroleum recovery industry. The petroleum refining industry needs better separation methods for the removal of acid gases, such as the removal of CO_2 and H_2S from natural gas containing between 15 to 50 percent acid gases and 50 percent or more CO_2 from large-scale enhanced oil recovery projects.

The temperature dependence of gas transport through the PMMA/PVDF films was investigated, for changes in temperature are well known to affect the physical properties of polymer membranes. Nevertheless, the transport properties of glassy polymer over a wide temperature range have been studied by only few research groups[2-7]. Changes in temperature always lead to modification of transport behavior and, sometimes, to loss of mechanical properties due to changes in morphology, degradation processes, cross-linking, etc. It also involves changes in polymer segmental mobility. The amount of those changes depends on the nature of the polymer and of the penetrant gas or liquid.

In the absence of defects, permeation through a polymer membrane usually is a solution-diffusion process, a combination of thermodynamic and kinetic factors. The permeability coefficient can be expressed as:

$$P = D\,S \tag{1}$$

where D = diffusion coefficient, a kinetic factor, and S = solubility coefficient, a thermodynamic factor.

If the permeability experiment is carried out over a temperature range in which no transitions in the polymer are observed (maximum temperature in this study is 40ºC lower than the T_g of PMMA) the temperature dependence of permeability, diffusion and solubility can be described by Arrhenius expressions for permeability and diffusion and a van't Hoff expression for solubility [7]:

$$P = P_0 \exp(-E_p/RT) \tag{2}$$
$$D = D_0 \exp(-E_d/RT) \tag{3}$$
$$S = S_0 \exp(-\Delta H_s/RT) \tag{4}$$

The combination of these equations shows that the activation energy for permeation, E_p, is the sum of the activation energy for diffusion and the heat of sorption:

$$E_p = E_d + \Delta H_s \tag{5}$$

Likewise, the pre-exponential factors (normally related to entropic factors) are defined as: $P_0 = D_0\,S_0$. For gases, the permeability usually is most governed by the kinetic components, E_d, and D_0 , since the thermodynamic components, ΔH_s and S_0, are relatively small.

2. Experimental

PMMA/PVDF films were prepared from separate solutions, using dimethylformamide as solvent for PMMA and acetone as solvent for PVDF. Two solution concentrations were used, 3%and 6% by weight, in order to obtain films with different thickness. The films were cast on glass plate and allowed to evaporate the solvents in a vacuum oven for 24 hours at 80ºC. The films were released from the glass plate and dried in a desiccator under vacuum overnight.

The films around 10 to 20μm thick, from the 3% and 6% solutions, respectively, were hydrolyzed at room temperature with 60% sulfuric acid solution for 1 hour, then washed with isopropanol and dried under vacuum for 24 hours before being analyzed. The final thicknesses of the films were 8 and 17μm, respectively.

The permeability experiments to calculate the coefficients of the transport parameters were performed by means of FTIR (Fourier Transform Infrared Spectrometry), which has been proven to be very reliable for the characterization of penetrant diffusion in polymers. This technique also can be used to calculate diffusion coefficients by the time-lag method. A Bomem MB-series FTIR spectrometer was used for this study. A special gas cell was placed inside the FTIR chamber for the permeation measurements, over a temperature range from 20 to 60°C. It was found that above that temperature the films undergo phase separation and loss of properties. By this technique, it is possible to calculate the diffusion coefficient without using high vacuum techniques requiring long degassing times. Nevertheless, a degassing of the film in a vacuum dessicator between experimental measurements is recommended, for a nitrogen flush between experiments sometimes is not sufficient to displace the sorbed gas within the film. This is true mainly for very condensable gases, such as CO_2 and even CH_4. Pure CO_2 and CH_4 and a 50/50 mixture of them were used in these experiments at a upstream pressure of 100kPa and a flow of 20ml/min.

3. Results and Discussion

For the thin 8 μm film, the permeation path length apparently is not enough to provide a significant separation between CH_4 and CO_2. For the thicker 17μm film, a marked decrease in permeability is observed for CH_4. The decrease in CO_2 permeability is not so pronounced (strongly marked). As the diffusive tortuosity factor increases with film thickness, the CO_2 molecule seems to require less energy to pass through the polymer matrix than do CH_4 molecules. Both penetrants have their mobility impaired by the increase of separation theoretical plates. In this case, one can say that for very thin films, thickness has an influence on permeability parameters. Thin films also have a greater probability of possessing flaws at a molecular level that might interfere with the transport separation of small molecules.

The permeabilities of the films increase with temperature, evidencing the kinetic and thermodynamic contribution to the overall transport process. Pure CO_2 permeabilities are found to be higher and increase at a higher rate than CO_2 mixed with methane. This is attributed to competition between the two gases of the mixture for sorption sites within the polymer matrix and possibly also with competition for "jump" sites, i.e., the polymer free volume that allows the diffusion of penetrant gas molecules. The hydrolyzed film surface presents higher polarity and higher cohesive energy density, favoring the sorption of CO_2 molecules and raising the activation energy for diffusion. Note, in Figure 1, that a lower difference exists between permeability coefficients of pure and mixed CO_2 but a considerable difference shows up between permeabilities of pure and mixed CH_4. The permeability values for the pure gases are greater in magnitude than for the gases in the 50:50 mixture.

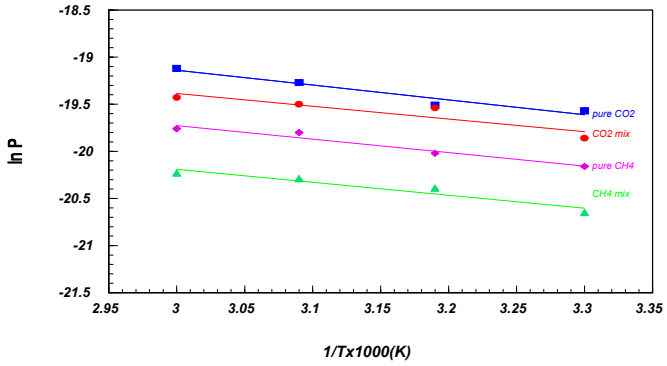

Figure 1. Arrhenius plot of temperature dependence of permeability coefficient (100kPa), for CH_4 and CO_2, through 8 μm hydrolyzed films.

Figure 2 presents the variations of CO_2/CH_4 gas mixture selectivities (α) with temperature. It is observed that the overall selectivity, $\alpha(P) = P(CO_2)/P(CH_4)$, increases slightly with temperature, different from non-hydrolyzed samples and from other glassy polymers. The kinetic diffusion selectivity, $\alpha(D) = D(CO_2)/D(CH_4)$, undergoes a slight increase with temperature. Being much more condensable than methane, CO_2 sorption is more influenced by the temperature increase than is CH_4. The thermodynamic solubility selectivity, $\alpha(S) = S(CO_2)/S(CH_4)$, presents an expected decrease. The solubility selectivity for the mixture of gases is much higher than the diffusivity selectivity, and decreases with temperature. However, this change takes place at a lower rate than the increase of the diffusion selectivity with temperature.

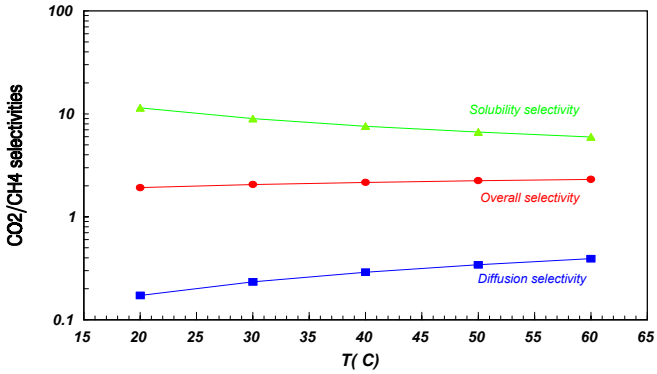

Figure 2. Temperature dependence of CO_2/CH_4 gas mixture selectivities (α) for 8μm hydrolyzed film .

Table 1 lists E_p, E_d and ΔH_s values for CO_2 and CH_4. It can be seen that E_p for pure CH_4 is slightly larger than for CH_4 mixed with CO_2. Since E_p is a combination of E_d and ΔH_s, it is inferred that CO_2 plasticizes the polymer matrix. It can be seen that the activation energy for diffusion for pure CO_2 is much lower than for CO_2 in the mixture with CH_4, as expected.

Table 1. Activation energies of permeation, diffusion and heat of sorption for CO_2 and CH_4 in 8 μm film.

Penetrants	E_p	(kcal/mol)	E_d	(kcal/mol)	ΔH_s	(kcal/mol)
	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4
Pure gas	1.60	1.30	3.40	1.80	-1.80	-0.50
Mixed gas	3.50	1.50	6.80	2.80	-3.30	-1.30

The dependence of CH_4 permeation on the plasticization effect of CO_2 explains the fact that, at higher temperatures, the separation factor is not as high as was otherwise expected.

Thicker films (17μm) also were analyzed. A longer path for transport of the penetrant molecules apparently imparts some different transport properties from the thinner films. Figure 3 presents the temperature dependence of CO_2/CH_4 gas mixture selectivities for these films. The overall selectivity decreases only a little with temperature, for the decrease in solubility is well balanced by the gain in CO_2 diffusion. The same trend as for the 8 μm films is observed in this case, but the overall selectivity is greater and the changes in the solubility selectivity and diffusivity selectivity with temperature are also greater than in the case of the thinner films.

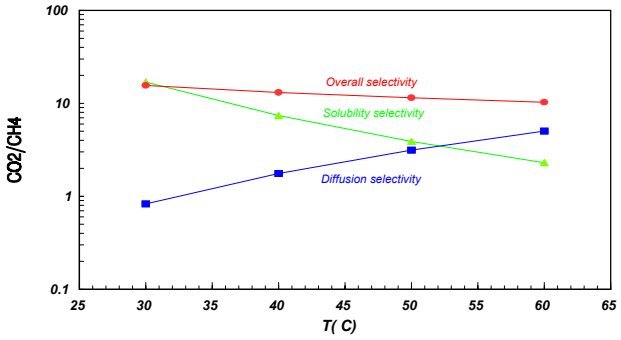

Figure 3. Temperature dependence of CO_2/CH_4 gas mixture selectivities (α) through 17μm hydrolyzed films.

Figure 4 presents Arrhenius plots of the temperature dependence of permeability coefficients for CO_2 and CH_4. In the gas mixture, while methane diffusion is improved due to the plasticization effect of CO_2, it seems that the presence of methane molecules impairs significantly the mobility of CO_2 molecules. Consequently, the sorption of CO_2 is less in the mixed system, but is still preferential in relation to methane. Methane sorption is greatly decreased in the case of the gas mixture.

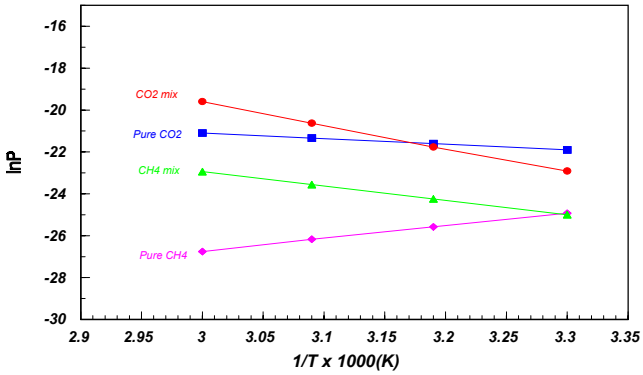

Figure 4. Arrhenius plot of temperature dependence for CH_4 and CO_2 permeability coefficients, pure and mixed, through 17μm hydrolyzed films (100kPa).

Table 2 presents the values for E_p, E_d and ΔH_s obtained for CO_2 and CH_4 in 17μm thick films.

Table 2. Activation energies of permeation, diffusion and heat of sorption for CO_2 and CH_4 in 17μm film.

Penetrants	E_p	(kcal/mol)	E_d	(kcal/mol)	ΔH_s	(kcal/mol)
	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4
Pure gas	5.30	-11.70	7.90	-10.40	-2.60	-1.30
Mixed gas	15.80	15.50	18.00	5.90	-2.00	9.60

4. Conclusions

The transport properties of carbon dioxide and methane gases, both pure and as a 50:50 mixture, were determined as functions of temperature in surface treated polyblends films of PMMA and PVDF. It was found that surface hydrolysis of part of the PMMA blend component, by H_2SO_4 solution, to poly(methacrylic acid) caused an increase in CO_2 permeation with lesser change in CH_4 permeation. This gave both an increase in the separation of the gas mixture and an increase in the yield flux of CO_2. It also was found that the separation efficiency was greater for the thicker membrane (17μm) than for the thinner membrane (8 μm) for nominally the same degree of surface region hydrolysis.

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5. Aknowledgments

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