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Dual-sorption model for H_2/CO_2 permeation in glassy polymeric Matrimid membrane

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ABSTRACT

This work deals with the membrane separation of hydrogen and carbon dioxide. Permeation experiments of pure and binary mixtures of H_2 and CO_2 were performed using the constant pressure technique and a planar membrane made of the commercial polyimide Matrimid 5218. For pure gases permeability values of 23.4 Barrer for hydrogen and of 5.2 Barrer for carbon dioxide were obtained leading to an ideal selectivity of 4.5 at 6 bar feed pressure. In the case of gas mixtures, H_2 permeability decreases with increasing contents of CO_2, while the permeability of carbon dioxide in mixtures presents similar values to pure gas permeabilities. As a result, the H_2/CO_2 selectivity obtained from mixed gas experiments decays to an average value of 3. The dual-sorption model with a partial permeant immobilization was used to predict each component permeation behavior for pure gases and binary mixtures. The carbon dioxide diffusion coefficients through the Matrimid polymer in the Henry and Langmuir mode were obtained, $D_{D,CO_2} = 2.14 \times 10^{-8}$ cm^2/s and $D_{H,CO_2} = 2.79 \times 10^{-9}$ cm^2/s. The model and the estimated parameters provide a reasonable agreement between experimental data and predicted permeability values with correlation coefficient $R^2 > 0.95$ and mean squared relative error (MSRE) lower than 0.01.

Keywords: Mixed gas separation; Matrimid membrane; Dual-sorption model

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1. Introduction

The introduction of hydrogen economy requires the development of efficient means to separate and retrieve hydrogen [1]. Today hydrogen production on a large scale is mostly through the steam reforming of methane, followed by the water gas shift reaction [2,3]. In addition, alternative and renewable resources for hydrogen production are proposed [4–9]. These involve biomass, water and carbohydrates rich, nitrogen deficient wastes such as solid (cellulose, starch), agricultural and food wastes. In the case of water and waste, bioprocess technologies like biophotolysis and anaerobic fermentation are being developed. The resulting product in all cases is a mixture of hydrogen with carbon dioxide and other minor gases. In spite of their high interest, the separation of hydrogen and carbon dioxide through membranes has not reached a commercial development. The main reason is related to the difficulty of combining a high hydrogen permeability and a low permeability to carbon dioxide.

For hydrogen separation, three types of materials can be used: inorganic-metallic, inorganic nano-porous (silica, ceramic, carbon, zeolite, oxide, glass) and organic polymeric membranes [10]. The choice between them must take into account the H_2 purity requirements for different applications and the temperature and pressure properties of the feed gas mixture. While fuel cell technology requires high purity hydrogen (minimum

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99.99%), hydrogen used as feedstock for hydro-cracking requires only 70–80% purity. The process gases rich in hydrogen that come from a thermochemical production process are at high temperature (the temperature of the second step of WGS is of 190–210°C). In this case palladium alloys are investigated to obtain ultrapure hydrogen even though these metals are too costly and evidence surface contamination by sulfur containing species. Meanwhile the biohydrogen that comes from water biophotolysis and waste anaerobic fermentation is at low temperature. Polymeric membranes are preferred when the operating conditions permit their usage because of their important benefits over inorganic membranes (lower material and fabrication costs, ease of processability, and capacity of long-term operation). Glassy polymers are the preferred materials for H_2 selective membranes since their rigid structures provide the capacity to discriminate molecules according to their size variation [11].

From the literature data [12], one can conclude that membranes based on polyimides provide an excellent selectivity in the separation of H_2/N_2, H_2/CH_4 and H_2/CO. H_2/CO_2 separation is more problematic, behavior assigned to the high solubility of carbon dioxide in polymers. Ideal H_2/CO_2 selectivities are calculated as the ratio of pure gas permeabilities, regardless membrane properties can be severely affected by a mixture of complex composition as that encountered in most off-gas streams. On the other hand, a notable decrease in hydrogen permeability when separated from mixtures containing carbon dioxide is expected, since it is documented that the higher the carbon dioxide concentration in the gas mixture, the higher the importance of membrane plasticizing phenomena [13]. To this date, the majority of the work related to the functional characterization of membrane materials is still carried out in single gas experiments rather than with gas mixtures even though is well accepted that single and mixed gas data will differ significantly [14].

In the present study, a commercial polyimide, Matrimid 5218, was chosen for the manufacturing of the membrane. This material has attracted a lot of attention for gas separation membranes due to the combination of relatively high gas permeability coefficients and separation factors coupled with excellent mechanical properties, solubility in non-hazard organic solvents and commercial availability [3]. The present study reports new gas permeability data for the commercially available and industrially applicable Matrimid 5218 membrane, related to gas mixtures of hydrogen and carbon dioxide and reveals specific phenomena to gas mixtures like solubility coupling and competitive sorption effects. Also, the "dual-mode sorption, partial immobilization" model was used to describe hydrogen and carbon dioxide permeation behavior for pure and binary mixtures. In this way new transport properties related to real process conditions are revealed. A reasonable agreement between predicted results and experimental data allows the satisfactory use of the resulted model to predict transport behavior of hydrogen and carbon dioxide in real mixtures.

2. Theoretical background

The transport, i.e., permeability P, of a gas through a dense polymeric film can be described as a solution–diffusion mechanism where the solubility S is a thermodynamic parameter and the diffusivity D is a kinetic parameter, Eq. (1)

$$P = DS \tag{1}$$

Gas sorption and diffusion in glassy polymeric membranes has been described by several established models but the use of the "dual-mode sorption, partial immobilization" theory has been more prevalent [13]. According to the dual-mode sorption model, gas sorption (C_m) in a polymer occurs in two types of sites, Henry and Langmuir sites, respectively. The first type is filled by gas molecules dissolved in the equilibrium free volume portion of the material (concentration C_D) and the second one corresponds to the population dissolved in the excess free volume of the glassy polymer (C_H) [12]. For a multicomponent gas mixture,

$$C_{m,i} = C_{D,i} + C_{H,i} = k_{D,i}p_i + \frac{c'_{Hi}b_ip_i}{1 + b_ip_i} \tag{2}$$

$$S_i \equiv \frac{C_{m,i}}{p_i} = k_{Di} + \frac{c'_{Hi}b_i}{1 + b_ip_i} \tag{3}$$

where, p_i is the partial pressure and k_{Di} represents the Henry law constant. c'_H is the Langmuir capacity constant that characterizes the total sorption capacity of the lower density regions (unrelaxed gaps) in a glassy polymer for a particular penetrant. The parameter b_i is the Langmuir affinity constant which characterizes the tendency of a given penetrant to sorb in the Langmuir mode. The primary effect for a mixture is the simple competition by the various penetrants for the excess free volume fraction of the polymer which causes a significant depression in sorption of all components of the mixture [13].

As a consequence of the existence of two types of adsorption sites in glassy polymeric membranes two diffusion coefficients can be defined. D_D is used for the mobility of the gas population dissolved in the polymer according to the Henry's law expression in the equilibrium free volume of the polymer and D_H for the mobility of the gas population contained in the excess free volume. The Fick's law expression for flux (J) through the membrane has the form:

$$J = -D_D\frac{dC_D}{dx} - D_H\frac{dC_H}{dx} \tag{4}$$

Substituting Eq. (2) into Eq. (4) and integrating from the high pressure to the low pressure across the membrane, one can get the permeability as follows, if D_D and D_H are constant and the downstream pressure is negligible [15].

$$P_i = k_{Di}\left(1 + \frac{F_iK_i}{1+\sum_{i=1}^{n} b_ip_i}\right)D_{Di} \tag{5}$$

where

$$K = \frac{c'_Hb}{k_D} \tag{6}$$

$$F = \frac{D_H}{D_D} \tag{7}$$

and p is the feed side pressure, K is a concentration sorption parameter and F can be viewed as the moving fraction of the Langmuir's population and the value $(1 - F)$ is always greater than 1.

Alternatively, Eq. (5) can be expressed in terms of component fugacity rather than partial pressures. The use of penetrant fugacity is clearly preferred as non-ideal gas phase mixture effects can be easily accounted for [16].

$$P_i = k_{Di}\left(1 + \frac{F_iK_i}{1+\sum_{i=1}^{n} b_if_{2i}}\right)D_{Di} \tag{8}$$

By fitting Eq. (8) with mixed gas experimental data of permeability versus gas partial pressure one can obtain diffusivities for the Henry's law and Langmuir mode.

3. Experimental

The commercial polymer Matrimid 5218 (polyimide of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride and diamino-phenylidene) was provided by Huntsman Advanced Polymers in powder form. Gases were purchased from Air Liquide (Spain) with a purity of at least 99.95%.

Film membranes, based on the polyimide Matrimid 5218, were prepared. After drying of the polymer powder at 120°C for 12 h, polymeric solutions (10–15 wt.%) were prepared by using dichloromethane (Panreac) as solvent. Thin films with an average thickness of 50 μm were obtained by solution casting on a glass plate using a casting knife (Elcometer 3580). The cast films were dried first at room temperature for 24 h and next in a vacuum oven (Selecta Vaciotem-T) at 120°C for 24 h and 200 mbar. The membrane sample had an effective membrane area of 12.13 cm^2.

Fig. 1 shows the permeation set-up used for the measurement of pure and binary mixtures (CO_2, H_2) gas permeabilities. The desired concentration of the feed mixture is obtained by controlling the flow rate of each gas with the mass flow controllers (Brooks 5850S). This gas mixture flows over the polymeric film mounted in the membrane test cell and leaves the system via the backpressure regulator (Brooks 5866). In the permeate side, where the pressure is maintained at atmospheric level the gas is removed with an argon sweep gas and introduced into a gas cromatograph (Agilent Micro GC 3000 – TCD detector), where the concentration of each component is determined.

For pure and mixed gas experiments, permeabilities P_i were calculated using Eq. (9)

$$P_i = \frac{Q_i\delta}{A\Delta p_i} \tag{9}$$

where Q_i is permeate flow rate for the component i, δ is the membrane thickness, A is the membrane area, Δp_i is the partial pressure gradient of component i through the membrane. Fugacities of the components were calculated using the Peng–Robinson equation. The separation factors were calculated as the ratio of permeabilities.

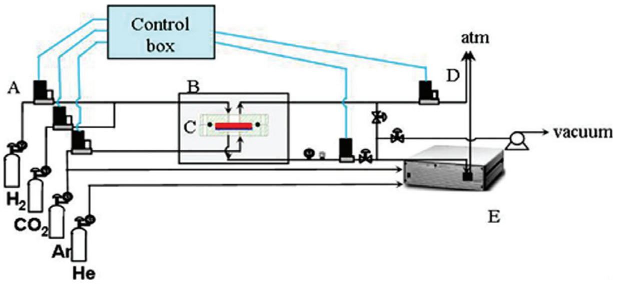

Fig. 1. The experimental permeation set-up: (A) Mass flow controller, (B) control box, (C) heating oven, (D) membrane test cell, (E) backpressure regulator and (F) gas chromatograph.

4. Results and discussion

The transport of pure carbon dioxide and hydrogen was studied at 2, 4 and 6 bar feed pressure at a temperature of 30 °C through Matrimid polymeric membrane. The resulting permeability values of 23.4 Barrer for hydrogen and 5.2 Barrer for carbon dioxide are in good correlation with literature data [17–20], Table 1, at a total feed pressure of 6 bar. As expected, hydrogen permeability presents a small decrease with pressure meanwhile the permeability of carbon dioxide presents a stronger decrease when pressure increases. Carbon dioxide transport is affected by pressure because is a more condensable gas and therefore more dependent of the solubility parameter that decreases when pressure increases. For pure gases the agreement with literature data validates the experimental procedure employed in this work.

In the case of binary gas mixtures of carbon dioxide with hydrogen a strong reduction in hydrogen permeability is observed with increasing values of CO_2 fugacity, as shown in Fig. 2. The depletion in H_2 permeability in the presence of CO_2 is related to the competitive sorption phenomenon between the two gases and is enhanced at increasing fugacity of CO_2 when more sorption of carbon dioxide in the Langmuir sites occurs because of carbon dioxide's larger affinity constant and solubility in glassy polymers. On the other hand, the permeability of H_2 is mostly independent on its own fugacity. For example, if we compare the experiments no. 2 and 8 collected in Table 1 (see also Fig. 2) where the CO_2 fugacity is kept practically constant (2.75 and 2.92 bar) and H_2 fugacity changes from 1.21 to 3.02, the H_2 permeability is almost constant (16.7 and 16.4 Barrers, respectively).

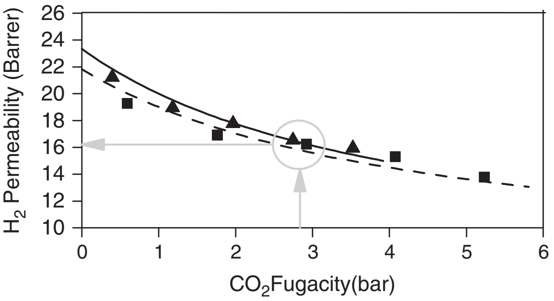

Fig. 2. H_2 Permeability vs. CO_2 fugacity obtained with feed binary mixtures H_2/CO_2, 30°C and Matrimid 5218 membrane. (▲) Experimental values of H_2 permeability, P_{total} = 4 bar; (■) experimental values of H_2 permeability, P_{total} = 6 bar; (- - -) model calculated values of H_2 permeability, P_{total} = 4 bar; (—) model calculated values of H_2 permeability, P_{total} = 6 bar.

As a consequence of the lower permeability of hydrogen in mixtures with carbon dioxide the real selectivity for the H_2/CO_2 gas pair, calculated from permeability data obtained in mixed gas experiments, decreases to an average value of 3, in the range of pressures 2–6 bars.

The transport data of pure carbon dioxide and hydrogen and their binary gas mixtures were fitted to the "dual-sorption partial immobilization model", Eq. (8), by nonlinear regression methods. To facilitate calculation, the gathering in smaller number of independent parameters was done as follows:

Table 1
Pure gas and binary mixtures H_2 and CO_2 permeabilities through a Matrimid membrane

Total pressure (bar)	Pure gas			Mixed gas					
	Permeability (Barrer)[a]		Ideal selectivity H_2/CO_2	Exp. no.	Fugacity (bar)		Permeability (Barrer)		Selectivity H_2/CO_2
	H_2	CO_2			H_2	CO_2	H_2	CO_2	
2	24.4	6.1	4.0	–	–	–	–	–	
4	24.0	5.5	4.4	1	0.41	3.53	16.2	5.4	3.0
				2	1.21	2.75	16.7	5.5	3.0
				3	2.01	1.97	17.9	5.8	3.1
				4	2.81	1.18	19.0	6.1	3.1
				5	3.60	0.40	21.2	6.9	3.1
6	23.4	5.2	4.5	6	0.61	5.23	14.1	5.2	2.7
				7	1.82	4.08	15.3	5.3	2.9
				8	3.02	2.92	16.4	5.5	3.0
				9	4.22	1.76	17.0	5.6	3.0
				10	5.41	0.59	19.3	6.2	3.1

[a] 1 Barrer = 10^{-10} $cm^3/s \cdot cm/cm^2/cmHg$.

$$A_1 = k_D D_D \tag{10}$$

$$A_2 = k_D FKD_D = D_H c'_H b \tag{11}$$

As a consequence the permeability parameters are defined as follows:

$$P_{H_2} = A_{1H_2} + \frac{A_{2H_2}}{1 + b_{H_2} f_{H_2} + b_{CO_2} f_{CO_2}} \tag{12}$$

$$P_{CO_2} = A_{1CO_2} + \frac{A_{2CO_2}}{1 + b_{H_2} f_{H_2} + b_{CO_2} f_{CO_2}} \tag{13}$$

The resulting system is composed of two equations with five independent parameters: A_{1H_2}, A_{1CO_2}, A_{2H_2}, A_{2CO_2}, b_{H_2}. Although the number of parameters is relatively high, the regression solution was unique due to the large domain of experimental data of permeability that in the case of P_{H_2} was in the range 13.7–24 Barrer. By substitution into Eqs. (10) and (11) of the known values of the sorption parameters of carbon dioxide in the Matrimid polymer [21]: $C'_{HCO_2} = 25.5$ cm^3/cm^3, $b_{CO_2} = 0.367$ 1/bar and $k_D = 1.42$ cm^3(STP)/cm^3/bar, at 35°C, we obtained the values of the CO_2 diffusion parameters in Henry mode $D_{D,CO_2} = 2.14 \times 10^{-8}$ cm^2/s and Langmuir mode 2.79 E-9 cm^2/s. These results fall in the same order of magnitude as previously reported values for glassy polymers [22]. We did not encountered published data for hydrogen solubility in Matrimid and therefore the final results are expressed as the grouped parameters $A_{1H_2} = 6.15$ Barrer, $A_{2H_2} = 21.31$ Barrer and $b = 0.06$ 1/bar. There is a reasonable agreement between predicted permeability values and experimental data, with correlation coefficient (R) higher than 0.95 and value of the mean squared relative error (MSRE) lower than 0.01, as it is exemplified by the plotted calculated lines shown in Fig. 2.

5. Conclusions

Pure gas permeability data are different from mixed gas permeability data. To be able to correctly design an industrial separation membrane system one should consider this aspect [12]. In the case of gas mixtures of hydrogen with carbon dioxide, hydrogen permeability is considerably lower than for pure gas meanwhile the permeability of carbon dioxide is unchanged resulting, therefore, an important decay in selectivity from an ideal value of 4.3 to a value of 3. This behavior was related to competitive sorption of the two gases in the polymer matrix and was satisfactorily described by the dual-sorption partial immobilization model. Therefore, this model can be used when designing the separation process as a useful tool to predict the permeability values at different partial pressures of the species.

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