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Behaviour of 1-hexyl-3-methylimidazolium chloride-supported ionic liquid membranes in the permeation of CO_2, H_2, CO and N_2 single and mixed gases

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ABSTRACT

The combined role of ionic liquids and membrane technology has demonstrated a tremendous potential in the field of gas separations; however, mostly single gas permeation data are available in literature and very few works report data regarding the membrane performance for the separation of gas mixtures. In this work, the performance of ionic liquid membranes prepared with the ionic liquid 1-hexyl-3-methylimidazolium chloride is assessed for the separation of binary, ternary and quaternary gas mixtures containing nitrogen, hydrogen, carbon monoxide and carbon dioxide. The mixed gas permeation properties of these gases are studied since they are the main components of flue gas generated after partial combustion of hydrocarbons. Therefore, the results obtained are compared to the pure gas permeabilities and ideal selectivities with especial interest on the effects on the recovery of H_2 and CO, which are the most valuable gases of the mixture. In summary, a decrease in all gas permeabilities is observed when dealing with gas mixture feeds, particularly, for the most soluble gas CO_2, due to a negative coupling effect. In contrast, the decrease in H_2 permeability, the least soluble gas, is less marked, and therefore its recovery is favoured. In addition, the effect of temperature on the single gas permeability is evaluated between 303 and 323 K.

Keywords: Permeability; Ionic liquid; Membrane; Gas separation; 1-hexyl-3-methylimidazolium chloride

1. Introduction

The use of ionic liquids has received a growing attention in the last decade in the field of separation technologies [1] and industrial catalytic reactions [2], among others, as an alternative to conventional organic molecular solvents. Room-temperature ionic liquids, being liquid salts composed of bulky asymmetric organic cations and anions that can be specifically combined to obtain the desired physical and chemical properties for a particular application, provide a wide variety of fascinating properties, e.g. negligible vapour pressure and non-flammability, high thermal and chemical stability, wide electrochemical

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window, excellent solvent properties, etc [3]. Ionic liquids have been studied as a unique platform for gas separation technologies, in particular, for carbon dioxide capture from the flue gases due to the extraordinary high affinity of CO_2 in ionic liquids compared to that of N_2 [4]. Nonetheless, it is worth mentioning that there are other industrial gas separations for which researchers have also focused on replacing the organic solvents commonly employed by ionic liquids, e.g. natural gas sweetening, hydrogen recovery and biogas upgrading [5].

Moreover, in the attempt to intensify these gas separation processes, membrane technology has shown high potential due to lower energy consumption, simplicity of operation and modularity compared to conventional gas separation technologies such as cryogenic distillation, pressure swing adsorption and absorption processes. For this reason, there is a great interest in combining ionic liquid and membrane technology, and the number of studies on this subject has exponentially grown in the last years [6]. Initially, the characterization of the gas permeation properties in ionic liquids was performed employing supported ionic liquid membranes (SILMs) prepared by immobilization of the ionic liquid into a porous polymeric or inorganic support [7]. Nowadays, researchers are focused on the development of more stable configurations, essentially by incorporating the ionic liquid into a polymer matrix that can be formed by either a conventional polymer with good mechanical and thermal properties (composite ionic liquid polymer membranes) [8] or a polymerized ionic liquid (poly(ionic liquid)-ionic liquid membranes) [9,10]. However, despite being less stable than the other configurations, SILMs can be readily prepared and thus represent a convenient way to characterize gas permeability through ionic liquids.

Regarding the use of ionic liquid membranes for gas separations, the vast majority of the published works only report data of single gas permeabilities and ideal gas selectivities. This information is necessary to determine which ionic liquids are the best candidates for a particular gas separation; however, it is also important to consider that the permeation properties of one gas may be altered by the presence of other gases in a gas mixture. For instance, Scovazzo et al. [11] reported mixed selectivities for CO_2/CH_4 and CO_2/N_2 gas pairs which slightly differed from the ideal gas selectivity; however, in that work, the permeabilities of the mixed gases were not calculated, and therefore it is not possible to determine if the gas permeation fluxes were modified when feeding gas mixtures. Also, Neves et al. [12] reported a small decrease in both mixed gas permeability of CO_2 and CO_2/N_2 and CO_2/CH_4 selectivities. In addition, other works report mixed gas permeation results for CO_2/N_2 separation [13,14] and olefin/paraffin separation [15,16].

In previous works, the recovery of valuable gases such as H_2 and CO from the flue gas stream obtained after a partial combustion of hydrocarbons in some industrial processes were sought by means of ionic liquid membrane technology [17,18] and chemical absorption process [19,20]. In those streams, N_2 was the major component together with H_2 and CO, and minor concentrations of CO_2 and other gases were also present. The ionic liquid employed for this purpose was 1-hexyl-3-methylimidazolium chloride, [hmim][Cl], since this ionic liquid can be used to synthesize a CO-selective ionic liquid that contains the same imidazolium cation but a series of chlorocuprate (I) anionic complexes [21,22] that selectively and reversibly react with CO [23].

Therefore, the aim of this work is to obtain mixed gas permeation data of CO_2, H_2, CO and N_2 through [hmim] [Cl] ionic liquid and then compare the results with the pure gas permeation of each gas so as to determine possible changes in the permeation behaviour of these gases. To that end, data of binary and ternary mixtures containing H_2, CO and N_2 were obtained in the first place, and then minor concentrations of CO_2 were added to the gas mixtures.

2. Experimental

A detailed description of the experimental set-up and procedures employed in this work can be found in Zarca et al. [17], which are briefly described in this section.

The ionic liquid employed throughout this work, 1-hexyl-3-methylimidazolium chloride, was purchased from Iolitec with a minimum purity of 99.5%. In order to determine the gas permeability through this ionic liquid, it was immobilized into a porous polymeric support. To that end, hydrophilic polyvinyledene fluoride membranes (Pall Corporation, 0.2-μm pore size) with a thickness (δ) of 129 μm were employed. The SILMs obtained were set between two hydrophobic polypropylene membranes (PolySep, 0.22-μm pore size) and eventually located over a porous metal frit into the permeation test cell.

The experiments were performed with either pure gases or gas mixtures that were prepared at the desired ratio by adjusting the individual mass flow controllers of each gas (Brooks 5850S). Moreover, a cylinder containing a plastic coil inside was placed before the test cell to assure gas mixing. In addition, a backpressure controller (Brooks 5866) was employed to set the feed pressure. In the permeate chamber, an argon gas stream was employed to sweep the permeate, and eventually, a gas chromatograph (Agilent 3000 Micro GC) was used to quantify the individual gas concentrations in the sweep gas (C_i). The accuracy of the chromatographic method was assessed with a gas mixture standard to be within 0.4%. Thereafter, the gas flux through the bulk ionic liquid ($J_{i,bulk}$) can be obtained from the permeate flow rate (Q_i) by taking into account the membrane area (A), which was 12.5 cm^2, and the characteristics of the porous support [24], porosity (ϕ) of 0.7 and a value of tortuosity (τ) of 3.0 [17], according to:

$$J_{i,bulk} = \frac{Q_i \times \tau}{A \times \phi} \tag{1}$$

where Q_i was determined by multiplying the experimental concentration of component i (% vol.) in the permeate stream, obtained by gas chromatography, by the sweep gas flow rate employed (4 cm^3 min^{-1}).

Finally, the gas permeability ($P_{i,bulk}$) can be calculated from the experimental permeate fluxes obtained at various pressure gradients with Eq. (2). The mean absolute error of replicated experiments in two different membranes was lower than 7% for each gas.

$$J_{i,bulk} = \frac{P_{i,bulk}}{\delta} \times \Delta P_i \tag{2}$$

Finally, the ideal selectivity ($\alpha_{i,j}$) was obtained from the ratio between the pure gas permeabilities as follows:

$$\alpha_{i,j} = \frac{P_{i,bulk}}{P_{j,bulk}} \tag{3}$$

3. Results and discussion

3.1. Pure gas permeation

In order to characterize gas permeation through the ionic liquid [hmim][Cl], the pure gases, N_2, CO, H_2 and CO_2, were fed individually to the membrane test cell and the permeate fluxes were determined. In this set of experiments, carbon dioxide permeation was analysed in the last place so as to avoid possible modifications of the other gas permeabilities; for instance, Cserjési et al. [25] reported a decrease in H_2 permeability between 15 and 30% after permeation of CO_2. In Table 1, the gas permeate fluxes obtained when the pressure gradient applied was varied between 1.5 and 2.5 bar are shown at a temperature of 303 K. A further increase in the applied pressure gradient resulted in a sharp raise of the permeate flux due to expelling of the ionic liquid from the porous support when the breakout pressure is reached. The gas permeability coefficients through the bulk ionic liquid can be calculated according to the steady-state gas flux equation (Eq. (2)) by fitting the experimental data of permeate flux vs. applied pressure gradient to a straight line that passes through the origin. A comparison of the gas permeabilities shows that CO_2 is the most permeable gas followed by H_2, CO and N_2, since the solubility of CO_2 in ionic liquids is at least one order of magnitude higher than that of the other gases [26,27]. In the case of H_2, its high permeability is due to the small kinetic diameter of the molecule (2.89 Å) that results in fast diffusion through the ionic liquid, despite being the least condensable gas of all the four [28]. Finally, CO has slightly higher solubility than N_2 in [hmim][Cl] [19] as well as comparable diffusivity, due to their similar kinetic diameters (3.76 and 3.64 for CO and N_2, respectively) [28]. Consequently, the CO permeability is barely higher than that of N_2, a fact that has also been observed in gas permeation through polymeric membranes [29].

Table 1
Pure gas permeate fluxes and gas permeability through 1-hexyl-3-methylimidazolium chloride at 303 K

ΔP (bar)	Permeate flux ($\times 10^7$ mol m^{-2} s^{-1})			
	N_2[b]	CO[b]	H_2	CO_2
1.5	6.9	13.4	66.3	197.8
2	9.1	18.7	87.7	264.0
2.5	10.6	22.1	113.3	320.7
Permeability (barrer[a])	6.0	11.8	67.7	212.1
Fitting to Eq. (2): R^2	0.96	0.98	0.99	0.99

[a] 1 barrer = 3.35 × 10^{-16} mol m m^{-2} s^{-1} Pa^{-1}.
[b] Data from [17].

Moreover, the effect of temperature on the gas permeability and selectivity has also been assessed for the three major compounds found in the flue gas stream. The permeability data obtained between 303 and 323 K are shown in Table 2, and in all three cases, the permeability increases at higher temperatures. Therefore, this fact indicates that there is a higher influence of temperature on gas diffusivity than on gas solubility, which usually has an opposite trend, i.e. solubility decreases as temperature is increased for CO and N_2

Table 2
Influence of temperature on gas permeability and selectivity

T (K)	Permeability (barrer)			Selectivity		
	N_2[a]	CO[a]	H_2	H_2/N_2	H_2/CO	CO/N_2
303	6.0	11.8	67.7	11.3	5.7	2.0
313	7.2	12.7	78.4	11.0	6.2	1.8
323	8.6	16.0	90.9	10.5	5.7	1.9
E_p (kJ mol^{-1})	12.4	14.7	12.0			

[a] Data from [17].

and it is almost not affected in the case of H_2 that presents a very low enthalpy of solvation as reported in several ionic liquids [27].

The effect of temperature can be well described by an Arrhenius-type equation [28]:

$$P = P_0 \, e^{-E_p/(R \cdot T)} \tag{4}$$

By plotting the natural logarithm of permeability vs. the reciprocal of temperature, the activation energy of permeation, E_p, can be obtained from the slope of the linear fitting of the data. These values, which are also shown in Table 2, indicate that N_2, CO and H_2 are similarly affected by temperature. Consequently, the calculated ideal gas selectivities at 303 K, 11.3 for H_2/N_2, 5.7 for H_2/CO and 2.0 for CO/N_2, do not change significantly when the temperature is increased from 303 to 323 K as shown in Table 2.

3.2. Mixed gas permeation

While data shown in the previous section only referred to pure gas permeation, in this section, results obtained with mixed gas streams are shown in order to account for possible deviations from the ideal gas selectivities due to different behaviours of the gases when they simultaneously permeate through an ionic liquid.

For this purpose, binary mixtures containing N_2, CO and H_2 were permeated in the first place. Since only minor concentrations of CO_2 are present in the flue gas under study, the effect of this gas is assessed in the following section. As can be seen from Table 3, the results obtained with binary mixtures revealed that the H_2 permeability slightly decreased, around 5–10%, with respect to the pure gas permeability. In contrast, the permeability of both CO and N_2 was remarkably reduced between 15 and 30% compared to the pure gas permeability.

Considering the thermodynamic and kinetic properties of these gases, the changes observed in the gas permeability of these gas mixtures may be rationalized in terms of a negative coupling effect, i.e. competition of the gases for a limited number of absorption sites in the ionic liquid phase [30,31]. While the superior H_2 permeability is mainly given by its fast diffusivity and, thus, it was not much affected by changes of the gas solubility, the permeability of the more condensable gases CO and N_2 decreased due to the coupling effect. This deviation from ideality has already been observed and attributed to changes in the solubility rather than in the diffusivity of the gases in rubbery PDMS membranes [32]. Accordingly, the mixed gas selectivity of H_2 towards CO and N_2 was increased to some extent, whereas the CO/N_2 mixed gas selectivity was similar to the ideal gas selectivity.

In the case of ternary mixtures with high content of N_2, analogous to that found in flue gas streams, the above-mentioned effects are also applicable, i.e. a slight decrease in H_2 permeability and a greater decrease in CO and N_2 permeability as shown in Table 3.

3.3. Effect of minor contents of CO_2

In this section, we evaluate whether the presence of CO_2 at low and medium concentrations can significantly alter the permeability of the gases that are in greater proportion in the gas stream. To that end, quaternary mixtures containing CO_2 from 5 to 20% were

Table 3
Mixed gas permeability and selectivity at 303 K

Gas mixture	Ratio (% vol.)	Permeability (barrer)			Selectivity		
		N_2	CO	H_2	H_2/N_2	H_2/CO	CO/N_2
CO/N_2	50/50	4.4	9.7	–	–	–	2.2
H_2/N_2	50/50	5.5	–	64.4	11.6	–	–
H_2/CO	50/50	–	8.6	62.4	–	7.3	–
$N_2/CO/H_2$	60/20/20	4.9	9.5	62.8	12.9	6.6	1.9

Table 4
Ideal selectivity and mixed gas selectivities of ternary and quaternary mixtures containing carbon dioxide (5–20% vol.) at 303 K

Feed gas composition $N_2/CO/H_2/CO_2$ (% vol.)	Selectivity		
	H_2/N_2	H_2/CO	CO/N_2
Ideal selectivity	11.3	5.7	2.0
60/20/20/0	12.9	6.6	1.9
55/20/20/5	13.6	7.5	1.8
50/20/20/10	13.4	8.4	1.6
55/15/15/15	13.2	8.9	1.5
50/15/15/20	14.0	8.9	1.6

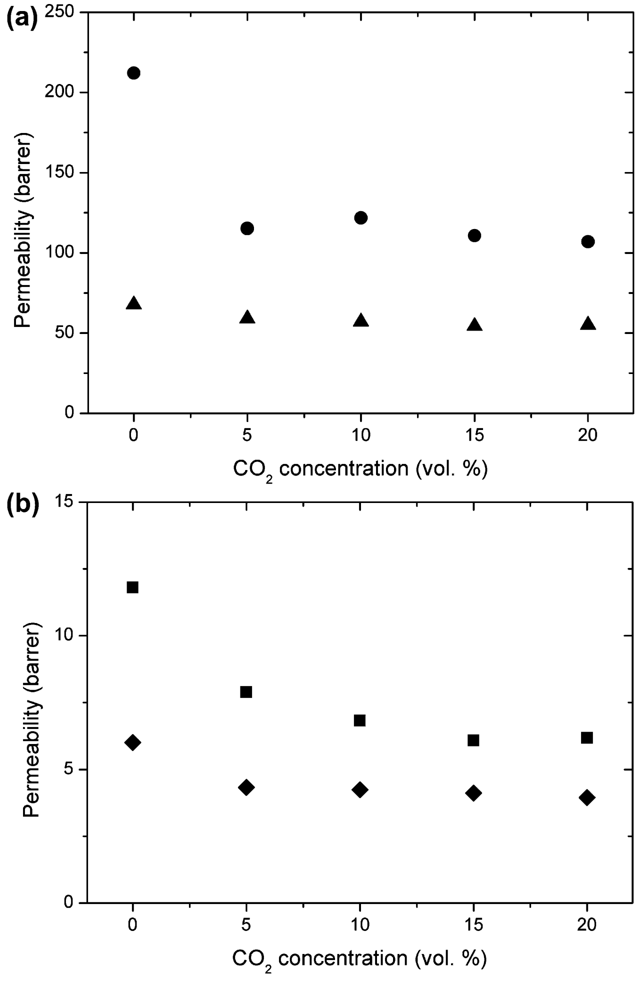

Fig. 1. Effect of carbon dioxide concentration on mixed gas permeability. (a) CO_2 (●) and H_2 (▲) and (b) CO (■) and N_2 (◆). Data corresponding to 0% vol. represent pure gas permeability.

fed into the permeation cell. The exact composition of each quaternary mixture can be seen in Table 4.

Fig. 1 shows the mixed gas permeability of CO_2, H_2, CO and N_2 obtained at increasing CO_2 concentrations. For comparison purposes, the data of the single gas permeability have also been included (0% vol.). The most remarkable effect is the drastic decrease in the CO_2 permeability, around 40–50%, compared to the single gas permeability. In addition, concerning the other gases, another 10–20% decrease in the gas permeability with respect to that obtained with ternary mixtures without CO_2 was also observed. This effect may also be ascribed to a competitive sorption in the ionic liquid, indicating that since CO_2 is the most soluble gas of all the four, it would also be the most affected gas by the presence of other condensable gases in the mixture.

Consequently, the H_2/N_2 and H_2/CO mixed gas selectivities increased with respect to both the ideal gas selectivity and that obtained with ternary mixtures without CO_2 as shown in Table 4, given that the decrease in H_2 mixed gas permeability was less marked. In contrast, the CO/N_2 mixed gas selectivity slightly decreased compared to the ideal gas selectivity.

4. Conclusions

In this work, data of single gas permeation and mixed gas permeation through the ionic liquid 1-hexyl-3-methylimidazolium chloride were systematically obtained for CO_2, H_2, CO and N_2 in order to assess the influence of gas mixtures composition on the permeation properties of each gas.

Results of pure gases show that CO_2 is the most permeable gas, due to its high affinity to the ionic liquid, followed by H_2, a fast-diffusing gas, and the less-soluble gases CO and N_2. The permeability of these gases was similarly affected by temperature and behaviour that can be described with Arrhenius-type equation with activation energies of permeation between 12 and 15 kJ mol^{-1}.

With respect to the mixed gas permeation results, binary and ternary mixtures composed of N_2, H_2 and CO revealed that the permeability of all gases decreased compared to the single gas permeability, especially for N_2 and CO, more soluble in [hmim][Cl] than H_2, due to a negative coupling effect. Consequently, a slight increase in the H_2 mixed gas selectivity towards both N_2 and CO was observed. These results suggest that the application of ionic liquid membranes for H_2 recovery would be benefited from mixed gas permeation.

Finally, the effect of minor CO_2 concentrations on the permeation properties of quaternary mixtures was assessed. In this case, the CO_2 permeability decreased to almost half the pure gas permeability, whereas the permeabilities of N_2, H_2 and CO barely decreased another 10–20% with respect to the permeabilities obtained with ternary mixtures. Therefore, this effect would be advantageous for the purpose of H_2 and CO recovery since the concentration of CO_2, the most permeable gas in the mixture, would decrease in the permeate stream.

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