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Gas permeation properties of 1-hexyl-3-methylimidazolium chloride supported liquid membranes

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Hydrogen and carbon monoxide are valuable gases of particular interest in the synthesis routes of a wide number of major chemical products; furthermore, H_2 is seen as a promising clean energy carrier and its application on fuel cells is in focus of research, however, highly pure H_2 is needed to avoid poisoning. The use of membrane technology is an important strategy on the way of process intensification in order to reduce the equipment size, energy utilization and production costs of conventional gas separation units, e.g., cryogenic distillation and adsorption processes [1]. The main applications in which H_2-permeable membranes for gas separations are presently applied are: H_2 recovery from ammonia purge gas streams, H_2/methane separation in refinery off-gas, and H_2/CO ratio adjustment in oxo-chemical synthesis plants. Another H_2 and CO source is the tail gas waste stream generated in the reactor of carbon black manufacturing industry, where these gases are present at concentrations up to 20 %vol. (on a dry basis) together with nitrogen (60%vol.), carbon dioxide (5%vol.) and other compounds in minor quantities [2]. The recovery of H_2 and CO from this source will lead to economic savings and a smaller environmental footprint.

Among the different membrane technologies, enhanced gas permeabilities can be expected in liquid membranes (LMs) since diffusivities in liquids are several orders of magnitude higher than in polymers. However, long-term stability and pressure in LMs represents the major challenges for development as they are still low, due to solvent evaporation or solvent displacement from pores at moderate transmembrane pressures. Room-temperature ionic liquids (RTILs) are organic salts that are liquid at ambient temperature and have a negligible vapor pressure, therefore, its use in supported ionic liquid membranes (SILMs) can overcome the instability problems associated with traditional solvents [3]. Furthermore, the properties of RTILs may be modified switching the cation or the anion to produce "task-specific" compounds. In addition, one of these ions has the potential to be -or become part of- a complexing agent, hence giving much greater loadings than standard solvent systems.

In a previous work [4], we designed an ionic liquid phase system for the recovery of CO from gaseous streams based on the ability of CO to form □ complexation bonds with copper (I) species. The liquid phase was obtained by the direct mixture of the ionic liquid 1-hexyl-3-methylimidazolium chloride ([hmim][Cl]) with the salt cuprous chloride (CuCl). The absorption experiments showed that the physical solubility of CO and N_2 in the pure [hmim][Cl] was almost negligible. On the contrary, the addition of CuCl to the ionic liquid enhanced CO solubility by a large factor owing to chemical sorption, whilst N_2 solubility remained very low. The thermodynamic equilibrium of the reacting system was also modeled, thus establishing the basis for a facilitated transport process to be used in supported liquid membranes.

In the present work, supported ionic liquid membranes were prepared in order to characterize the permeate fluxes of the single gases N_2, H_2, and CO, and its binary and ternary mixtures, through the supported pure ionic liquid ([hmim][Cl]) as a previous step to perform permeation experiments through supported mixtures of the ionic liquid with cuprous chloride. Moreover, mixed gas experiments with quaternary mixtures were carried out to study the effect of CO_2 feed gas concentration on gas permeabilities. In addition, the effects of temperature (293 – 323 K) and transmembrane pressure (1.5 – 2.5 bar) were examined as well.

SILMs were prepared employing a pressure immobilization procedure [5] in two steps: first, membranes were soaked with the ionic liquid in a vacuum oven for a few hours; secondly, membranes were placed in a stainless steel cell and a feed N_2 flux was applied until N_2

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permeance reached steady state conditions. The supporting material is a microporous (0.2 μm pore size) hydrophilic PVDF membrane (Pall Corp.), with a thickness of 129 μm.

Gas permeation experiments were performed using the experimental set-up and procedure that have been described in a previous work [2]. SILMs were arranged between two microporous hydrophobic polypropylene membranes adopting a sandwich configuration into a stainless steel test cell. Then, a feed gas flow was applied and the desired feed gas concentration was regulated through individual mass flow controllers. The permeating compounds were removed by an argon sweep gas stream and their concentrations were analyzed via gas chromatography. Standard deviations of measurements are shown in graphics as error bars.

Fig. 1 shows pure gas fluxes through the membrane as a function of the pressure gradient applied in the range between 1 and 2.5 bar. A linear dependency is observed for all four gases, thus permeability coefficients were calculated at 303 K: P_{CO2} =378.6 x 10^{-18}, P_{H2} =112.0 x 10^{-18}, P_{CO} =19.9 x 10^{-18} and P_{N2} =13.1 x 10^{-18} m^3 (STP) m s^{-1} m^{-2} Pa^{-1}.

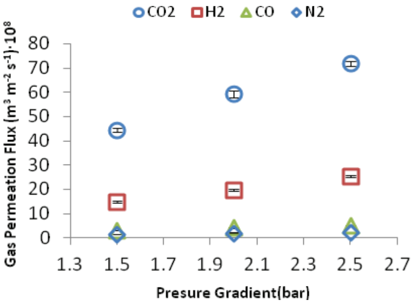

Fig. 1. Permeation flux of four gases in [hmim][Cl] SILM, T = 303 K.

Temperature effect on gas permeability (Fig. 2) was almost negligible for CO and N_2. In contrast, H_2 permeability strongly increased with temperature. These results may be explained in terms of the opposite effect of temperature on gas solubility (exothermic process) and diffusivity (enhanced by higher temperatures), which are balanced in the case of CO and N_2, and in terms of a great influence of temperature on hydrogen diffusivity, as all three gases has similar solubilities in this ionic liquid. On the other hand, mixed gas experiments carried out with binary and ternary mixtures of H_2 with low permeable gases N_2 and CO showed no significant changes on their permeabilities compared to the values obtained with pure gases. However, the presence of CO_2 in quaternary mixtures with H_2, N_2 and CO determined a depression in gas permeabilities as CO_2 concentration was increased. The results showed that gas permeabilities through the [hmim][Cl] supported liquid membrane are in the low range of gas permeabilities reported through other SILMs [6].

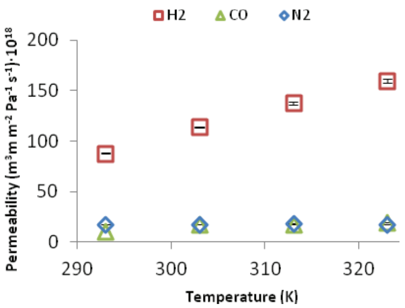

Fig. 2. Temperature effect on gas permeability. SILM prepared by impregnation of [hmim][Cl] on microporous PVDF.

This research is focused on the recovery and valorization of the tail gas stream generated in the production of carbon black. In a previous work, H_2 recovery by means of polymeric membranes has been studied. In this work, new gas permeability data of H_2, N_2, CO and CO_2 through pure [hmim][Cl] SILM are reported. N_2 and CO permeabilities are low and, as expected, similar. Thus, the selective recovery of CO would require the enhancement of carbon monoxide flux. We propose the incorporation to the SILMs of a CO selective carrier, i.e., cuprous chloride, which has proven to provide solubility selectivity over N_2.

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