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**IONIC LIQUID-BASED MEMBRANES WITH
ENHANCED CARBON MONOXIDE
SEPARATION PROPERTIES**

**(Membranas basadas en líquido iónico con
propiedades mejoradas para la separación de
monóxido de carbono)**

Para acceder al Título de

Graduado/a en Ingeniería Química

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TÍTULO	IONIC LIQUID-BASED MEMBRANES WITH ENHANCED CARBON MONOXIDE SEPARATION PROPERTIES		
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KEYWORDS

Carbon monoxide, ionic liquid, membrane, gas separation, solution-diffusion model, copper (I) thiocyanate, 1-ethyl-3-methylimidazolium.

SCOPE

Carbon monoxide, CO, gaseous in normal atmospheric conditions (15° C and 101.3 kPa), is a colorless, odorless, and highly toxic gas [1]. Environmental regulations and concerns are strong incentives to reduce the amount of CO released to the atmosphere. However, carbon monoxide has a large number of applications. Conventional industrial CO production methods are harmful processes for the environment [2]. In this work, membrane technology was applied as a promising alternative to recover CO from existing industrial gas mixtures due to their efficacy, reduced energy requirement and operating costs. However, membrane separation of CO from N₂-rich gas mixtures is a separation problem due to their similar solubility and diffusivity properties in most of the available polymers [3].

Supported ionic liquid membranes (SILMs) were developed in order to take advantage of the outstanding properties of ILs, such as negligible vapor pressure, non-flammability, higher thermal stability and easy recycling with potentially lower energy demand, that may provide new opportunities in CO separation processes [4]. Nevertheless, the use of SILMs is normally not feasible at elevated process temperatures due to the resulting decrease in ionic liquid viscosity and at elevated pressures, in which the capillary forces that retain the ionic liquid in the pores of the support are overcome. These operation conditions can lead to increased loss of ionic liquid from the membrane support during operation.

To overcome these stability problems associated with SILMs, thermally-stable composite ionic liquid and polymer membranes (CILPMs) were synthesized, in which

the ionic liquid is trapped within the polymer chains, so that the stability of the ionic liquid in the membrane is considerably improved [5].

RESULTS

SILMs were performed by immersion of a porous polymer support into the ionic liquid (IL) [EMIM] [SCN] plus vacuum process. SILMs were also performed by adding copper (I) thiocyanate as a selective carrier for CO separation. CILPMs were also obtained by solvent casting process by dissolving [EMIM] [SCN] and a polymer into a proper solvent. In terms of adding the copper salt in the CILPM, it should be noticed that finding an appropriate solvent to dissolve the selected polymer, IL and copper salt, represented a huge challenge. After many attempts for achieving the proper solubilization, PEBAX-CILPMs were obtained by dissolving all compounds in a solvent mixture of n-butanol and Tetrahydrofuran (THF).

After SILMs and CILPMs preparation, membrane separation properties were measured by gas permeation tests performed at different conditions of temperature and pressure for the following gases: H₂, N₂, CO and CO₂. These tests were performed for both types of membranes with either pure gases or gas mixtures. For pure gases, N₂ and CO permeability coefficients were equal to 3.8 and 5.4 barrers respectively, and CO/N₂ selectivity value was 1.42 for pure IL-SILMs at 303 K. However, the permeability coefficients were 2.7 and 5.3 barrers for N₂ and CO, respectively, and the CO/N₂ selectivity value was 2.1 for copper(I) containing-SILMs at 303 K. Regarding IL-based PEBAX CILPMs results, the permeability coefficients were 8.7 and 14.2 barrers and the CO/N₂ selectivity value was 1.6 at 1.3 bar. Finally, permeability coefficients were 5.1 and 10.6 barrers and the CO/N₂ selectivity value was 2.0 for copper (I)-containing PEBAX-CILPM at 1.3 bar and 303 K.

CONCLUSIONS

After the accomplishment of the present work the following conclusions were established:

1. Pure [EMIM] [SCN]-SILMs reached low CO and N₂ permeability and CO/N₂ selectivity.

2. Copper (I)-containing SILMs shown a significant improvement for gases separation due to higher CO/N₂ selectivity values as temperature and copper content increased.
3. Selectivity values were higher employing pure gases than mixed gases as the feed resource.
4. CILPMs presented a linear behavior of permeabilities as driving force was increased according to solution-diffusion model and membrane plasticization was not observed. As the ionic liquid content increased, gas permeabilities and CO/N₂ selectivity increased too.
5. Copper (I) containing-CILPMs were obtained dissolving the target ionic liquid, PEBAX polymer and copper (I) salt in a mixture of n-butanol and THF achieving partially-fully solubilisation.
6. Copper (I) containing- PEBAX CILPMs achieved lower values of permeability than pure IL PEBAX CILPMs ones and CO/N₂ selectivity values did not change with temperature.

Thus, copper incorporation in the CILPMs with the target ionic liquid of this work could not be practically considered as a way to further enhanced membrane separation properties.

7. This problem could be analyzed in future works characterizing the membrane with one of the characterization methods suggested in this work in order to determine components distribution through the membrane.

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PALABRAS CLAVE

Monóxido de Carbono, líquido iónico, membrana, permeación de gases, modelo de solución-difusión, tiocianato de cobre (I), 1-etil-3-metilimidazolio.

PLANTEAMIENTO DEL PROBLEMA

El monóxido de carbono, CO, gaseoso en condiciones atmosféricas normales (15 °C y 101,3 kPa), es un gas incoloro, inodoro y altamente tóxico [1]. Las regulaciones y preocupaciones ambientales son fuertes incentivos para reducir la cantidad de CO liberado a la atmósfera. Sin embargo, el monóxido de carbono tiene un gran número de aplicaciones. [2]. En este estudio, la tecnología de membranas se aplicó como una alternativa prometedora para recuperar el CO de las mezclas de gases industriales existentes debido a su eficacia, reduciendo los requerimientos energéticos y los costos de operación. Sin embargo, la separación por membrana de CO de mezclas de gases ricos en N₂ es un reto debido a sus propiedades similares de solubilidad y difusividad en la mayoría de los polímeros disponibles [3].

Se desarrollaron membranas de líquido iónico soportadas para aprovechar las excelentes propiedades de los líquidos iónicos, tales como presión de vapor despreciable, no inflamabilidad, mayor estabilidad térmica y fácil reciclaje con una demanda energética potencialmente más baja, lo que puede proporcionar nuevas oportunidades en procesos de separación de CO [4]. Sin embargo, el uso de estas membranas no es factible a elevadas temperaturas del proceso debido a la disminución resultante en la viscosidad del líquido iónico, ni a altas presiones ya que se superan las fuerzas capilares que retienen el líquido iónico en los poros del soporte, lo que puede conducir a una pérdida de líquido en el soporte de membrana durante su funcionamiento. Para superar estos problemas de estabilidad, se sintetizaron membranas térmicamente estables compuestas de líquido iónico y polímero, en las que el líquido iónico queda atrapado dentro de las cadenas poliméricas, de manera que la estabilidad del líquido iónico en la membrana es mejorada [5].

RESULTADOS

Las membranas de líquido iónico soportadas fueron preparadas por inmersión de un soporte polimérico poroso en el líquido iónico [EMIM] [SCN] seguido de un proceso de vacío. Éstas también se realizaron añadiendo tiocianato de cobre (I) como portador selectivo para la separación de CO. Las membranas compuestas se sintetizaron mediante un proceso de casting mediante la disolución de [EMIM] [SCN] y un polímero en un disolvente adecuado. En cuanto a la adición de la sal de cobre en la misma, debe destacarse que encontrar un disolvente apropiado para disolver el polímero seleccionado, el líquido iónico y la sal de cobre, representó un gran desafío. Después de muchos intentos para conseguir la solubilización apropiada, se obtuvieron membranas de PEBA disolviendo todos los compuestos en una mezcla de n-butanol y Tetrahidrofurano (THF). Después de la preparación de las membranas, se midieron las propiedades de separación de membrana mediante pruebas de permeación de gases realizadas en diferentes condiciones de temperatura y presión para los siguientes gases: H₂, N₂, CO y CO₂. Estos ensayos se realizaron para ambos tipos de membranas con gases puros o mezclas de gases. Para gases puros, los coeficientes de permeabilidad de N₂ y CO fueron 3,8 y 5,4 barrers respectivamente, el valor de selectividad de CO/N₂ fue de 1,42 para la membrana soportada con líquido iónico a 303 K. Sin embargo, los coeficientes de permeabilidad fueron 2,7 y 5,3 para N₂ y CO, respectivamente, y un valor de selectividad fue de CO/N₂ de 2,1 para las membranas soportadas con sal de cobre (I) a 303 K. Respecto a los resultados de membranas compuestas de PEBA, se obtuvo 8,7 y 14,2 barrers de permeabilidad y un valor de selectividad de CO/N₂ de 1,6 a 1,3 bar. Finalmente, se obtuvieron coeficientes de permeabilidad de 5,1 y 10,6 barrers y un valor de selectividad de CO/N₂ de 2,0 para las membranas compuestas de PEBA que contenía sal de cobre (I) a 1,3 bar y 303 K.

CONCLUSIONES

Después de la realización del presente trabajo se establecieron las siguientes conclusiones:

1. Las membranas soportadas con líquido iónico obtuvieron bajas permeabilidades de CO y N₂ y selectividad de CO/ N₂.
2. Las membranas soportadas que contenían sal de cobre (I) mostraron una mejora significativa para la separación de gases debido a mayores valores de

- selectividad de CO/N₂ a medida que aumentaba la temperatura y el contenido en cobre.
3. La selectividad fue más alta empleando una alimentación de gases puros en vez de mezclas.
 4. Las membranas compuestas de PEBAX presentaron un comportamiento lineal de las permeabilidades de acuerdo con el modelo de solución- difusión y no se observó plastificación de la membrana. A medida que aumentaba el contenido de líquido iónico, aumentaron también las permeabilidades de los gases y la selectividad de CO/N₂.
 5. Se obtuvieron membranas compuestas que contenían cobre (I) disolviendo el líquido iónico objetivo, el polímero PEBAX y la sal de cobre (I) en una mezcla de n-butanol y THF logrando una solubilización prácticamente total.
 6. La membrana compuesta de PEBAX que contenía sal de cobre (I) obtuvo valores de permeabilidad inferiores a las compuestas de líquido iónico puro y los valores de selectividad CO / N₂ no presentaron cambios con la temperatura. Por lo tanto, la incorporación de cobre en las membranas compuestas con el líquido iónico objeto de estudio no podría considerarse prácticamente como una forma de potenciar las propiedades de separación de membrana.
 7. Este problema podría ser analizado en un futuro caracterizando la membrana con uno de los métodos de caracterización sugeridos en este trabajo con el fin de determinar la distribución de los componentes a través de la membrana.

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1. Introduction

Carbon monoxide, CO, gaseous in normal atmospheric conditions (15°C and 101.3 kPa), is a colorless, odorless, and highly toxic gas. [1]

Considerable amounts of carbon monoxide enter the atmosphere from the combustion of fossil fuels and from natural processes (i.e., oxidation of methane emitted by decaying organic matter). Thus, substantial concentrations of CO can be detected in the air of major urban areas, primarily due to emissions from vehicle exhausts and domestic heating.

Environmental regulations and concerns are strong incentives to reduce the amount of CO released to the atmosphere. However, carbon monoxide has a large number of applications as a raw material.

Major applications are as a reducing agent for the production of metals, in the production of hydrogen by the water-gas shift reaction, and for the carbonylation of organic substrates such as alcohols, amines, and esters. Also, mixtures of hydrogen and carbon monoxide (syngas) are used as feed-stocks of growing importance for the large-scale production of several chemicals such as methanol and aliphatic alcohols and aldehydes (oxo synthesis). [2]

The industrial production of CO is mainly based on the gasification of coal or the reforming of natural gas or petrochemical products. These are harmful processes for the environment. Therefore, it is convenient to replace them by CO separation processes from existing gas mixtures.

All sources of CO are essentially gas mixtures with two primary components, CO and hydrogen. CO usually is rejected together with other gases, mainly nitrogen (N₂) and carbon dioxide (CO₂).

Gas purification techniques fall into four main categories: cryogenic processes, adsorption process, liquid absorption and membrane processes.

Regarding the cryogenic separations, these processes essentially consist of liquefaction of part of the fuel stream, followed by a phase separation and distillation of the remaining liquid components. This method is the oldest, and two principal methods can be used in large-scale processes depending on the required purity: partial condensation cycle and methane wash cycle. The disadvantage of cryogenic processes is that they are only suitable for large capacity and high purity CO plants where the nitrogen content of the purified CO stream is tolerated by the downstream application.

Adsorption processes, also known as pressure swing adsorption (PSA), consist of passing the syngas mixture (H_2/CO) sequentially through first and second adsorptive beds, each of which adsorbs H_2 more readily than CO. Typically, a minimum of three adsorptive beds are used, as the process involves three cyclical steps: production (selective adsorption), regeneration of the adsorber (evacuation of the adsorbed gas), and repressurization of the bed with a portion of the purified stream. The number of beds is increased for higher flow rates or higher CO recovery rates.

The adsorption process is suited to the production of high purity product with a high yield of CO.

Liquid absorption processes are based on the selective and reversible complexation of CO with metal-based complexing compounds in a liquid solution. One of the most important is the COSORB process; it works well to produce high-purity CO from a variety of gas mixtures, including a nitrogen-rich feed.

The last two methods of separation are easier and more economical than cryogenic distillation, particularly if N_2 is present in the feed stream, but continue to be costly and energy-intensive. [1]

Finally, Membrane technology is seen as a promising alternative to the traditional separation processes because of their efficacy, and reduced energy requirement and operating costs.

Usually permselective membranes are employed such as carbon membranes and polymeric membranes. However, membrane separation of CO from N₂-rich gas mixtures is a separation problem due to similar solubility and diffusivity properties of these two gases in most of the polymers. [3]

This drawback leads us to propose new alternatives in the processes of gas separation improving membrane technology for CO separation.

1.1 Ionic liquids (ILs) definition

Ionic liquids, ILs, are organic salts that are composed entirely of ions and are fluid below 100 °C. Because ILs are liquids at low temperatures they are also often called room temperature ionic liquids (RTILs).

ILs consist of large bulky and asymmetric organic cations and inorganic or organic polyatomic anions.

The radical (R group) of the cation is variable, typical, alkyl chains such as methyl, ethyl, butyl, etc., but can also be any of a variety of other functional groups. The variability of the anion and R groups in the imidazolium, pyridinium, pyrrolidinium, ammonium or phosphonium cations may be used to adjust the properties of the ionic liquids. So, properties, such as the IL melting point, viscosity, and solubility of starting materials and other solvents into ILs, are determined by the substituents on the organic component and by the counterion. [4]

These property effects are listed in **Table 1**.

Table 1. Properties of Ionic liquids according to the ions influence.

	Melting Point	Density	Viscosity	Thermal stability
General information	Below 100 °C	Ranging from 1 to 1.6 g/cm ³	Ranging from 10 mPa·s to 10,000 mPa·s at room temperature.	Thermally stable up to 500 °C
Cation influence	Large cations and increased asymmetric substitution results in a melting point reduction.	Decrease with an increase in the length of the alkyl chain in the cation.	Alkyl chain lengthening in the cation leads to an increase in viscosity.	No influence, it is limited by strength heteroatom-carbon and their heteroatom-hydrogen bonds.
Anion influence	The increase in anion size leads to a decrease in melting point.	Also affected by the identity of anions.	The ability of anions to form hydrogen bonding has an effect on viscosity.	Thermal stability of ionic liquids containing dicyanamide or tricyanomethide anions is significantly lower than might be expected.

In this way, a vast range of ionic liquids can be created. The number of possible combinations of anions and cations is rapidly increasing.

In general, Ionic liquids possess the following desirable properties:

- Liquidus range of 300 °C (-96 ± 200 °C)
- Excellent solvents for organic, inorganic, and polymeric materials
- Acidic compositions are superacids (pKa ≈ 20)
- Some are water-sensitive; others are hydrophobic and air-stable
- High thermal stability and high ionic conductivity
- Easy to buy and simple to prepare
- No measurable vapor pressure, nonflammable
- Exhibit Brønsted, Lewis, Franklin, and 'super'acidity
- Highly solvating – therefore low volumes used, implying process intensification
- Catalysts as well as solvents
- Highly selective reactions [4]

These properties enable their use in many fields. **Figure 1** shows the main fields of ionic liquids application.

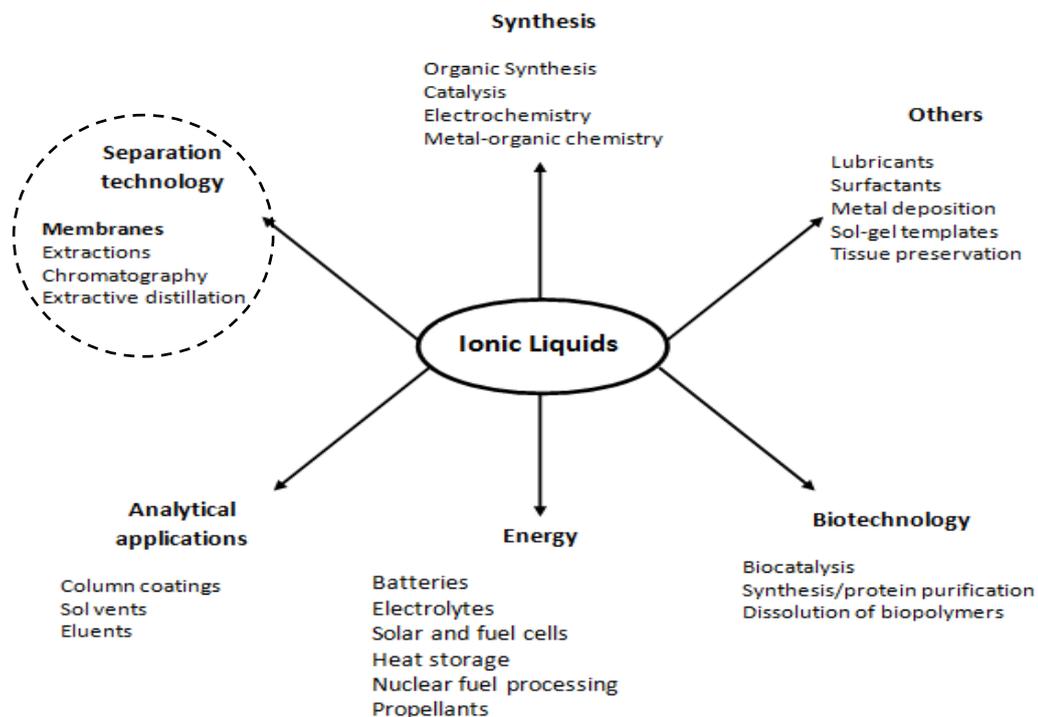


Figure 1. Main fields of application of Ionic Liquids (ILs) [5]

In the membrane separation field, some of the above features can provide new opportunities in CO separation processes, such as negligible vapor pressure, non-flammability, higher thermal stability and, ease of recycling with potentially lower demand for energy in the solvent regeneration step compared to traditional volatile organic solvents. This implies more energy efficient and environmentally friendly gas separation processes.

However, the disadvantages of ILs include high viscosity, high production costs, unclear toxicities and potential environment effects (i.e., they are non-biodegradable), which limit their further industrial application. [6]

1.2 Supported ionic liquid membranes (SILMs)

A supported (or immobilized) liquid membrane (SLM) is a non dispersive-type liquid membrane, in which the liquid-phase selective material is immobilized into the pores of a porous support by capillary forces.

Gas transport in an SLM involves three steps, as shown in **Figure 2**: gas molecules from feed side dissolve in the liquid phase of the SLM, diffuse through the SLM, and release to the permeate side of the SLM.

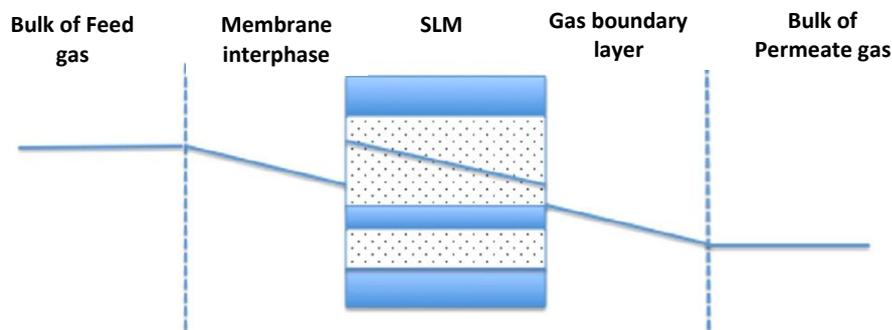


Figure 2. Gas transport in a SLM.

If an Ionic Liquid is used in SLMs, the membranes are called SILMs. A SILM is a liquid membrane system in which the IL is held by capillary forces in the pores of a support material. The support materials mainly include polymeric and inorganic membranes. [6]

The use of SILMs for gas separation has been widely studied in the last decade. Due to the fact that the diffusion of species in liquids is faster when compared with diffusion in solids, it is expected that the permeability across liquid membranes becomes higher than when using solid polymer membranes. [7]

1.2.1 SILMs preparation processes

In general, there are three main methods for the preparation of SILMs, direct immersion, vacuum and pressure, which can play an important role on the operation performance of SILMs due to the relatively high viscosity of ILs.

For the direct immersion method, immobilization of IL takes place by soaking the support material in the IL under atmospheric pressure. Then, the excess IL should be removed from the material surface either by leaving to drip overnight or by drying softly with a tissue.

This method is the easiest way in comparison with the other two methods.

For the vacuum method, the SILMs can be obtained as follows. Firstly, the support material is placed inside a vacuum-tight chamber for a certain time in order to remove air from the pores of the material. Then, IL is scattered at the membrane surface while keeping vacuum in the chamber. Finally, the excess IL on the surface of membrane should be removed in the same way than the other method.

For the pressure method, the immobilization of IL is performed by the following steps: (1) placing the material in an ultrafiltration unit, (2) adding an amount of IL in the unit, (3) applying a certain nitrogen pressure to force the IL to flow into the pores of the material, (4) releasing the pressure once a thin layer of IL was apparent on the surface of the membrane, and (5) removing the excess IL on the membrane surface. [6]

In **Table 2** are listed some examples of ILs and supports used in SILMs for the three conventional methods.

Table 2. Examples of ILs and material supports used in SILMs. [6]

IMMOBILIZATION METHOD	MATERIAL SUPPORT	ILs
Immersion method	Hydrophilic PVDF membrane	six phosphonium-based ILs
	Hydrophobic PP film	[BMIM]PF ₆
	Different membranes (i.e. Fluoropore, Durapore, Mitex).	100% solution of ILs (eight imidazolium, one phosphonium and one ammonium-based ILs)
Vacuum method	4 hydrophilic membranes with equal nominal pore size, (PP, PVDF, Nylon and PES)	[BMIM][PF ₆] and [OMIM][PF ₆]
Pressure method	Nylon organic membrane	[BMIM][Cl], [BMIM][BF ₄] or [BMIM][NTf ₂]

A research has been made for new methods of preparation of SILMs performed in recent years to see the evolution of the technique compared to traditional methods. This research, shown in **Table 3**, includes the target gases to be separated and the size of the membrane pore.

Table 3. Research of new techniques of SILMs preparation.

REFERENCE	IMMOBILIZATION METHOD	MATERIALS SUPPORT	PORE DIAMETER	APPLICATION
Hernández-Fernández, 2009	Immersion followed by a vacuum process.	Nylon (Poliamide) hydrophilic	0.45 μm	Selective separation of gas mixtures
Cheng, 2014	Vacuum drying, incorporation of IL to ambient temperature and vacuum heating.	Assymetric and simmetric PVDF	0.22 μm	CO ₂ / N ₂
Couto.R, 2015	Pressure method in a high pressure stainless steel vessel introducing CO ₂	Polyvinylidene fluoride (PVDF) hydrophobic	0.22 μm	CO ₂ / N ₂ and CO ₂ / O ₂
Zhongde Dai , 2016	Immersion method followed of vacuum to remove gas bubbles in resulting membranes.	Al ₂ O ₃	20 nm	CO ₂ separation
M. Yahia, 2017	IL Injection inside the pores after vacuum in a desiccator.	Polyvinylidene fluoride (PVDF) hydrophobic	0.22 μm	CO ₂ / N ₂
Yongli Sun, 2017	Vacuum drying, permeated cell and N ₂ pressure	Polyvinylidene fluoride (PVDF) hydrophilic	0.1 μm	Ethylene/ethane mixture

1.2.2 SILM characterization processes

Since the properties of different membrane parts, such as the surface or the cross section, are very important for practical applications, it is important to have the means to characterize and measure those structures and properties. In fact, surface characterization is not only important for understanding the relationship between the membrane structure and its properties but also for guiding surface modification.

It is well known that various aspects of a membrane surface, which include chemical composition, morphology and topography, wettability, and biocompatibility, can affect the properties and applications remarkably. Many kinds of characterization techniques may be applied to study the surface properties of a SILM. [8]

Characterization techniques can be classified into static and dynamic techniques. The static techniques mainly give information on membrane morphology and structure, chemical and physical properties. The dynamic techniques are of fundamental importance when investigating membrane performance. Some characterization techniques are destructive for the membrane, while the non-destructive ones are applied also to monitor the membrane performance during its use. [9]

Table 4 shows the main methods used for SILMs characterization and the membrane information that each methodology provides.

Table 4. Main SILMs characterization methods.

CHARACTERIZATION	METHOD	APPLICATION
SEM	The membranes are frozen in liquid nitrogen, broken to obtain the cross section and coated with gold prior to SEM observation.[9]	Morphological structure of the resultant membranes
SEM-EDX	A scanning electron microscope (SEM) ISI DS-130 coupled to a Kevex Si/Li detector and a Sun SparcStation for energy-dispersive X-ray (EDX) analysis is used. [10]	Characterize the membrane surface morphologically and examine the global chemical composition of the membranes and the distribution of the ILs within them. (analysis of chemical elements of atomic number higher than Be)
Impedance spectroscopy (IS)	Impedance spectroscopy measurements of the SILMs, placed between two aqueous solutions, are carried out at regular time intervals to understand the impact of the presence of water microenvironments on the electrical properties of the SILMs.[11]	Determine the electrical properties of the supported ionic liquid membranes, such as the electrical resistance and capacitance under working conditions, i.e., in contact with saline solutions.

<p>X-ray photoelectron spectroscopy (XPS)</p>	<p>The supported liquid membranes are analyzed immediately after preparation and after 1 week's immersion in de-ionised water. A Physical Electronics spectrometer is used, with X-ray Mg K radiation (300 W, 15 kV, 1253.6 Ev aprox.) as the excitation source.</p> <p>Membranes are mounted on a sample holder without adhesive tape and kept overnight at high vacuum in the preparation chamber before being transferred to the analysis chamber of the spectrometer for testing.[12]</p>	<p>Chemical characterization of the surface of the supported liquid membranes</p>
<p>Thermogravimetric analysis (TGA)</p>	<p>TGA analyses are performed using a thermal analyzer in a N₂ atmosphere. The scan is carried out at constant heating rate at temperatures from the room temperature to 1000 K. [13]</p>	<p>Determination of thermal properties</p>

As explained above, SILMs have many advantages to be used in gas separation processes by improving both permeability and selectivity. However, the use of such supported ionic liquid membranes is normally not feasible at elevated process temperatures and pressures due to the resulting decrease in ionic liquid viscosity, which can lead to increased loss of ionic liquid from the membrane support during operation. [14]

To overcome these stability problems associated with SILMs, thermally-stable composite ionic liquid and polymer membranes (CILPMs) are being developed.

In CILPMs, the ionic liquid and the polymer are dissolved in a solvent and the solution is cast and dried on a flat surface to fabricate CILPMs. In this way, the ionic liquid is trapped within the polymer chains, so that the stability of the ionic liquid in the membrane is considerably improved while keeping the separation properties of the IL.

1.3 Goal and scope

In this work, different types of ionic liquid-based membranes were developed and tested in order to achieve a selective and competitive alternative method for the separation of CO from N₂ that may lead to significant energy and investment costs savings with respect to conventional gas separation processes.

In particular, the following tasks are addressed in this work:

- Preparation of SILMs using the target ionic liquid [EMIM][SCN] and adding copper(I) thiocyanate as the selective carrier for CO separation.
- Synthesis of CILPMs with different polymers and solvents for the proper solubilization of the target ionic liquid and the copper salt.
- Gas permeation experiments for both types of membranes in order to obtain high permeability and selectivity values of different gases such as CO, N₂, H₂ and CO₂.

2. Theoretical Background

The gas transport through either a SILM or a CILPM is usually described in terms of the **solution-diffusion mechanism**, in which gas solute dissolves in the membrane material at the feed side and then diffuses through the membrane down to the permeate side due to a concentration gradient.

The separation is achieved between different gases because of differences in the amount of material that dissolves in the membrane and the rate at which the material diffuses through the membrane. [15]

The flux per unit pressure gradient, known as permeability coefficient (P_i) is defined as the product of the solubility coefficient (S_i) times the diffusion coefficient (D_i) of the gas molecule.

Permeability coefficient of component 'i' is defined by **Equation 1**.

$$P_i = S_i \cdot D_i \quad \text{(Equation 1)}$$

The ratio of permeabilities for a gas mixture of components 'i' and 'j', is the membrane selectivity ($\alpha_{i,j}$).

Therefore, it can also be expressed as the product of the ratio diffusion coefficients (diffusivity selectivity) times the ratio of solubility coefficients (solubility selectivity).

Equation 2 shows the equivalence in the definition.

$$\alpha_{i,j} = \frac{P_i}{P_j} = \frac{S_i}{S_j} \cdot \frac{D_i}{D_j} \quad \text{(Equation 2)}$$

Under steady state conditions and assuming diffusion and solubility coefficients to be independent of concentration, the gas permeation flux (J_i) can be defined as the expression shown in **Equation 3**.

$$J_i = D_i \cdot S_i \cdot \frac{\Delta p_i}{\delta} = P_i \cdot \frac{\Delta p_i}{\delta} \quad \text{(Equation 3)}$$

Where $\frac{\Delta p_i}{\delta}$ is the applied pressure gradient across the membrane thickness. Gas permeation flux units in the S.I are $\left[\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right]$.

The gas permeability of a membrane is often expressed in Barrer, where:

$$1 \text{ Barrer} = 10^{-10} \left[\frac{\text{cm}^3(\text{STP})}{\text{cm} \cdot \text{s} \cdot \text{cm Hg}} \right] = 3.35 \cdot 10^{-16} \left[\frac{\text{mol} \cdot \text{m}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}} \right]$$

3. Materials and Equipment

Experimental setup and materials were used in this work in order to test two types of membranes prepared, SILMs and CILPMs, for gas permeation processes.

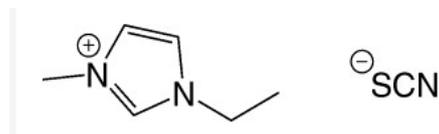
3.1 Materials and reagents

Polymers

- Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)
- Polyacrylonitrile (PAN)
- Polyether block amide (PEBAX)

Ionic Liquid

1-Ethyl-3-methylimidazolium thiocyanate >98 %
[EMIM] [SCN]



Main properties:

- Empirical formula: $C_7H_{11}N_3S$
- Molar mass (M) :169,247 g/mol
- Density (D): 1,119 g/cm³
- Melting point (mp): -6 °C

Solvents

- Acetone (C_3H_6O)
- N-Methyl-2-pyrrolidone (NMP) (C_5H_9NO)
- Tetrahydrofuran (THF) (C_4H_8O)
- n-butanol ($C_4H_{10}O$)
- i-propanol (C_3H_8O)

Reactant

Copper (I) thiocyanate (>99%)

3.2 Equipment

The experimental setup, employed in this work to perform the gas permeation tests for the above mentioned two types of membranes, was based on a continuous operation under steady-state conditions.

This experimental facility, depicted in **Figure 3**, consisted of five pure gas cylinders (N_2 , H_2 , CO , CO_2 , Ar) as the feed and carrier gases. Each cylinder is controlled by an individual mass transport flow controller, which is in charge of the feed composition regulation, and by a pressure indicator.

Also, a gas mixer was placed before the test permeation cell in case the feed gas was a gas mixture.

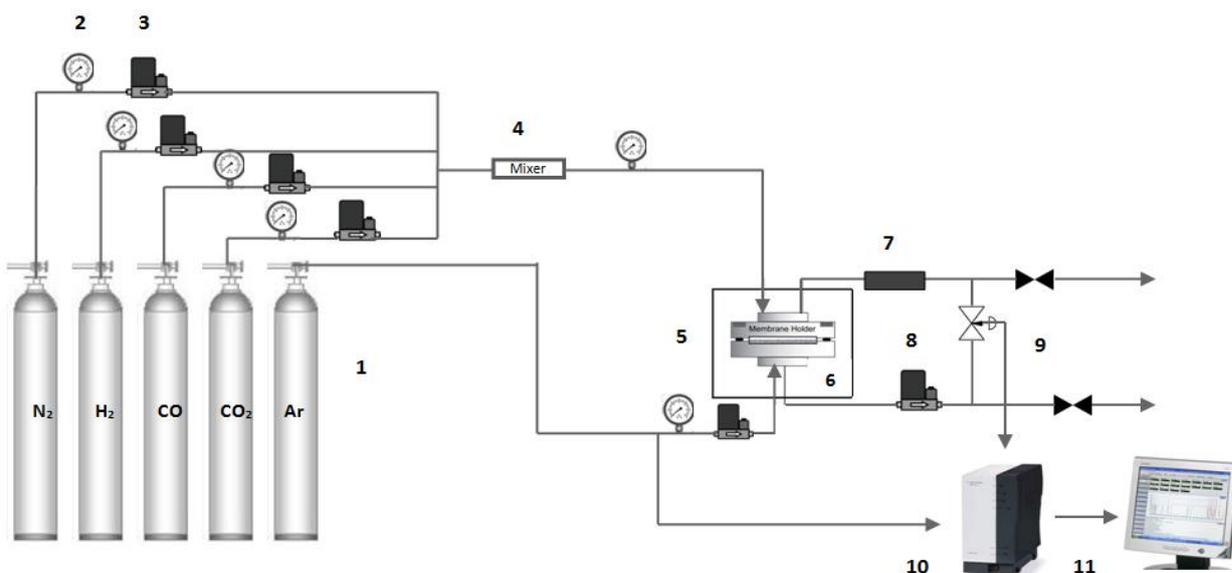


Figure 3. Scheme of the experimental setup: (1) gas cylinders, (2) Pressure indicators, (3) mass flow controllers, (4) gas mixer, (5) heating oven, (6) permeation cell, (7) pressure transducer, (8) gas mass flowmeter, (9) valves, (10) gas chromatograph, (11) OpenLAB CDS EZChrom software.

The permeation cell, shown in **Figure 4**, was inside a heating oven in order to control operation temperatures. The cell had two inputs (carrier gas and feed gas) and two outputs (retentate and permeate) connected to the setup with four tube connections.

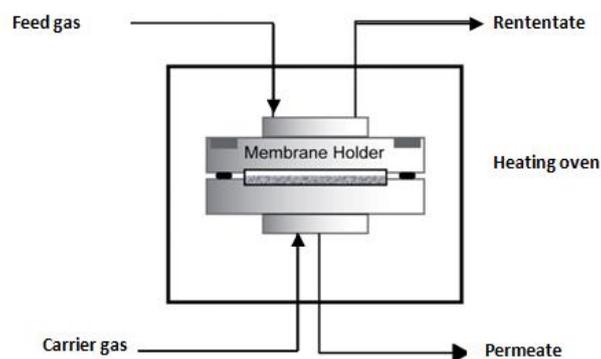


Figure 4. Schematic gas permeation cell.

The two output tube connections were connected to different parts of the setup. The retentate stream is connected to a pressure transducer in order to control the pressure in the chamber.

The permeate stream, which was removed by the sweep gas (Ar), was connected to a gas chromatograph in order to determine the concentration of each gas. All the results obtained in the chromatograph are saved and plotted in a control program identifying each gas according to its retention time.

All technical and commercial information about each equipment is collected in **Table 5**.

Table 5. Equipment Technical data

EQUIPMENT	MODEL/ MATERIAL	PARAMETERS
Individual mass controllers	Brooks 5850S	0-100 cm ³ (NTP) min ⁻¹ flowrate
Permeation cell	Stainless steel	12.5 m ² area
Tube connections	Stainless steel	1/8 inch.
Back pressure regulator	Brooks 5866	0-20 bar
Gas mass flow meter	Brooks 5850S	4 cm ³ (NTP) min ⁻¹ flow rate
Gas chromatograph	Agilent 490 Micro GC	Concentration, 1 ppm to 100 % level
Control Program	OpenLab Control Panel, microGC	-

4. Methodology

As explained above, two different approaches have been followed in this work to prepare IL-based membranes for CO separation. (i) Supported Ionic liquid membranes (SILMs) and (ii) Composite Ionic Liquid and Polymer Membranes (CILPMs).

4.1 Preparation of SILMs

Supported ionic liquid membranes were prepared with the room temperature ionic liquid (RTIL) 1-ethyl-3-methylimidazolium thiocyanate [EMIM] [SCN] and the polymeric polyvinylidene fluoride (PVDF) microporous membrane (FP-Vericel, 0.2 μm pore size, 47 mm diameter) as the material support.

The PVDF membrane thickness was determined using a digital micrometer (Mitutoyo digimatic micrometer, 0-25 mm, ± 0.001 mm accuracy) being the average value 137 μm . Some of the SILMs were also prepared with cuprous thiocyanate salt as the selective compound for CO separation.

To prepare the SILMs, first of all, IL was dissolved in the cuprous thiocyanate salt by mechanical stirring providing heat during few minutes in case of adding the salt. In case of pure IL soaking, this step is neglected.

Then, PVDF membrane supports, cut to a 45 mm diameter circle, were soaked in the IL at room conditions. After impregnation, the excess IL was removed from the material surface by leaving to drip at 30 °C and 10 mbar of pressure inside a vacuum chamber (Vaciotem-T, -1 bar) during 1 hour.

Once the SILMs were prepared, SILMs were placed over a hydrophobic polypropylene membrane (PolySep, 0.1 μm pore size, 47 mm diameter), previously cut at the same diameter, to prevent IL leakage from the membrane pores.

4.2 Preparation of CILPMs

Composite ionic liquid and polymer membranes were prepared also with the room temperature ionic liquid (RTIL) 1-ethyl-3-methylimidazolium thiocyanate [EMIM] [SCN] and three different polymers: Poly (Vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), Polyacrylonitrile (PAN) and Polyether block amide (PEBAX).

Thus, the solvents used in the membrane preparation were different depending on the chosen polymer according to solubility preferences. Cuprous Thiocyanate (CuSCN) salt was also added to some of them to perform the selective separation of gases.

As it is explained above, CILPMs were prepared by dissolving the polymer in a solvent magnetically stirred and providing small amounts of heat.

Once the polymer was totally dissolved, the ionic liquid was added at the same time than the copper salt and the solution magnetically stirred for 1 hour in case of adding the salt.

This procedure was done to assure a proper solution of the three membrane components. If pure IL-CILMP was prepared, the IL was added at the same time than the polymer.

The duration of the stirring process relies on the chosen polymer due to their differences in boiling point and solubility values. Then, the homogeneous mixture was cast in a vacuum chamber.

CILPMs thicknesses were measured with a digital micrometer (Mitutoyo digimatic micrometer, 0-25 mm, ± 0.001 mm) obtaining different values detailed below.

5. Results and discussion

Gas permeation tests were performed at different conditions of temperature and pressure for the following gases: H₂, N₂, CO and CO₂. When the membrane was placed in the permeation cell properly, a N₂ gas stream was initially applied in order to remove moisture from the SILM and assure that steady permeate flux was achieved.

The tests were performed for both types of membranes with either pure gases or gas mixtures. The gases volume concentration in the permeate stream were determined from their peak area obtained by the thermal conductivity detector in the gas chromatograph.

It was necessary to take into account that CO₂ should be measured in the last position in order to avoid the phenomenon of plasticization during the permeation of CO₂ in amorphous polymers, that modifies the rate of permeation and membrane selectivity.

Once this information was known, the permeability of each gas through the membrane expressed in Barrers was calculated according to **Equation 4**.

$$P_i = \left(\frac{Q_i \cdot \delta}{A \cdot \Delta p_i} \right) \cdot 10^{10} \quad \text{(Equation 4)}$$

Where:

A : Membrane area expressed in cm^2

δ : Thickness of the membrane expressed in cm

Δp_i : Partial gradient pressure expressed in mmHg (1 bar= 75.006 mmHg)

Q_i : Permeate flow rate in cm^3/s

Q_i was calculated as follows in **Equation 5**.

$$Q_i = C_i \cdot Q_{\text{carrier}} \quad \text{(Equation 5)}$$

Where, C_i is the concentration of the component i in the permeate stream expressed in volume percentage and Q_{carrier} is the permeate flow rate of the carrier gas expressed in ml/s. The permeate flow rate of the carrier gas was 4 ml/s in all tests performed.

Once the permeability was calculated, molar permeate flux was defined as it is shown above in **Equation 3**.

5.1 Gas permeation through [EMIM] [SCN] – SILMs

SILMs prepared with [EMIM] [SCN] ionic liquid by immersion plus vacuum method were tested with pure feed gases at different temperatures from 303 to 323K obtaining the gas permeation results listed in **Table 6**.

Table 6. Gas permeation results through [EMIM][SCN]-SILMs as a function of temperature

Temperature (K)	P (Barrers)			α (CO/N ₂)	α (H ₂ /N ₂)
	N ₂	H ₂	CO		
303	3.8	12.1	5.4	1.42	3.18
313	4.5	14.6	6.3	1.40	3.24
323	5.3	17.3	7.6	1.43	3.26

As can be seen in **Table 6**, the permeability of each gas increases as temperature is increased. It can be explained in terms of an increase of gas diffusion higher than the gas solubility decrease.

This temperature dependence can be described by Van't Hoff-Arrhenius equation, linearized in **Figure 5** in order to obtain the activation energy of permeation, which is the slope of the plot according to **Equation 6**.

$$\ln P = \ln P_0 - E_p/RT \quad \text{(Equation 5)}$$

Where, E_p is the apparent activation energy of permeation and R is the ideal gases constant.

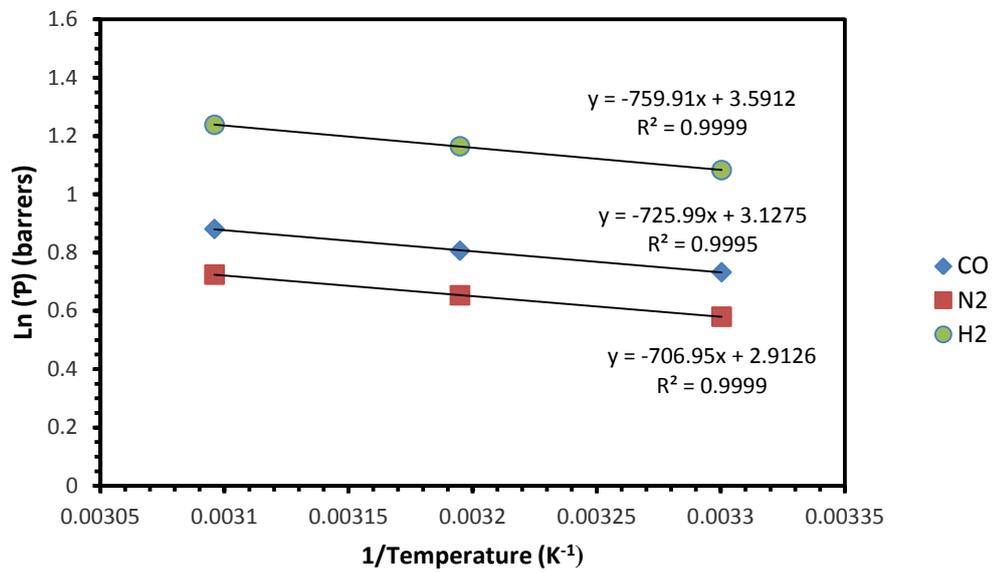


Figure 5. Logarithm of CO, N₂ and H₂ permeability vs. the inverse of temperature

According to the linearized equations, the E_p values of N₂, CO and H₂ are 5.8, 6.0 and 6.3 kJ/mol, respectively.

Consequently, as can be seen in **Figure 6**, CO/N₂ and H₂/N₂ selectivities do not increase with temperature, the values remain practically constant due to their similar activation energies of permeation.

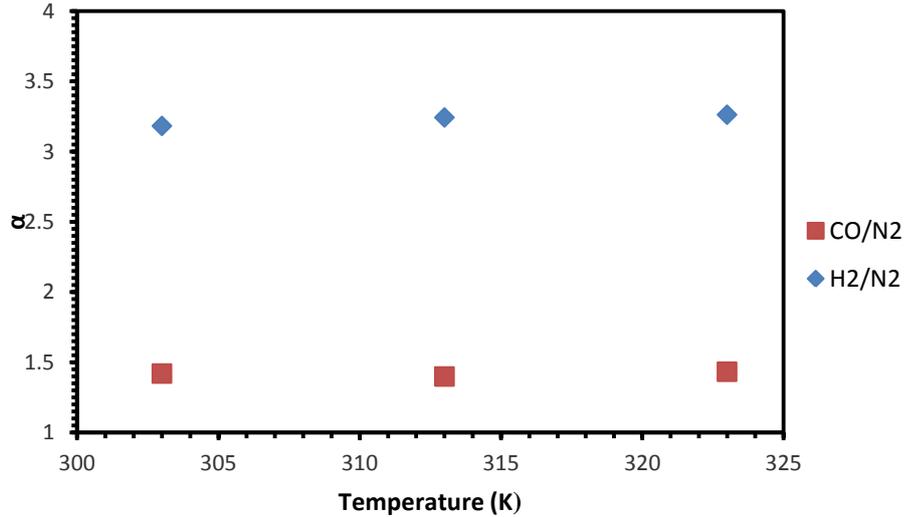
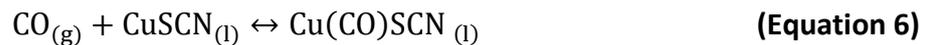


Figure 6. CO/N₂ and H₂/N₂ selectivity behavior through [EMIM][SCN]-SILM with pure feed gas.

5.2 Gas permeation through copper (I) thiocyanate-containing SILMs

SILMs were prepared with two different concentrations of CuSCN in [EMIM][SCN] for the purpose of ascertain if copper(I) thiocyanate salt acts as a selective carrier for CO separation according to the following reversible complexation reaction (**Equation 6**).



The molar ratios of copper salt to ionic liquid used were 0.11 and 0.24, which correspond to a 20 and 30 percent of molar content of copper in the ionic liquid, respectively.

Gas permeation tests at different temperatures were performed in order to verify whether the ideal selectivity is promoted by an increase in temperature. The driven force applied was a partial pressure gradient of 1.3 bar given that the sweep gas stream leads to a permeate partial pressure equal to 0; thus the flux is calculated according to **Equation 3**.

As can be seen in **Table 7**, which collects gas permeabilities obtained through the copper (I)- containing SILMs from 303 to 323 K at 1.3 bar of driving force, N₂ and H₂ permeability coefficients decreased in comparison with pure [EMIM][SCN] -SILMs results. However, CO permeability values slightly increased. Thus, CO/N₂ selectivity was enhanced in this type of membranes.

Gas permeability coefficients through copper (I) - containing SILMs increased as the temperature was increased too. This behavior occurs due to the decreasing IL viscosity.

N₂ and H₂ permeability coefficients also presented a small decrease by the increase in copper salt molar concentration, while CO permeability coefficients remained practically constant. This effect can be explained by a reverse effect in which CuSCN addition can restrict diffusivity and decrease gas permeability.

Table 7. Gas permeability results through copper (I)- containing SILMs as a function of temperature and copper concentration at 1.3 bar with pure feed gases

CuSCN/[EMIM][SCN]	Temperature(K)	P (Barrers)		
		N ₂	H ₂	CO
0.11	303	2.7	8.9	5.3
	313	3.2	10.9	6.8
	323	3.9	15.4	8.4
0.24	303	2.4	6.5	5
	313	2.6	8.5	5.7
	323	3.2	10.9	7.2

Table 8 shows gas selectivity results through both copper (I) - containing SILMs from 303 to 323 K at 1.3 bar of driving force. As can be noticed, H₂/N₂ and H₂/CO selectivities have slightly smaller values in comparison with pure IL-SILMs results. This effect was also observed when temperature and copper (I) concentration was increased. This behavior can be explained because CO permeation is favored as temperature and copper salt content increase.

Table 8 . Gas selectivity results through copper (I)- containing SILMs as a function of temperature and copper concentration at 1.3 bar with pure feed gases

CuSCN/[EMIM][SCN]	Temperature(K)	α		
		CO/N ₂	H ₂ /N ₂	H ₂ /CO
0.11	303	1.9	3.3	1.7
	313	2.0	3.4	1.6
	323	2.2	3.9	1.8
0.24	303	2.1	2.7	1.3
	313	2.2	3.2	1.5
	323	2.3	3.4	1.5

The CO/N₂ selectivities of both copper (I) containing-SILMs prepared as a function of temperature are plotted in **Figure 7**. A significant increase of selectivity in comparison with pure [EMIM] [SCN]-based SILM is observed, due to the increasing solubility of CO into the IL while the reaction with the copper (I) salt takes place.

It is also appreciated an increase of CO/N₂ selectivity as temperature and copper concentration increases; this effect implies an improvement in relation to the above explained [EMIM] [SCN] - based SILM results, which do not present this behavior, thus indicating an influence of the reversible complexation reaction on the CO gas permeability via facilitated-transport mechanism.

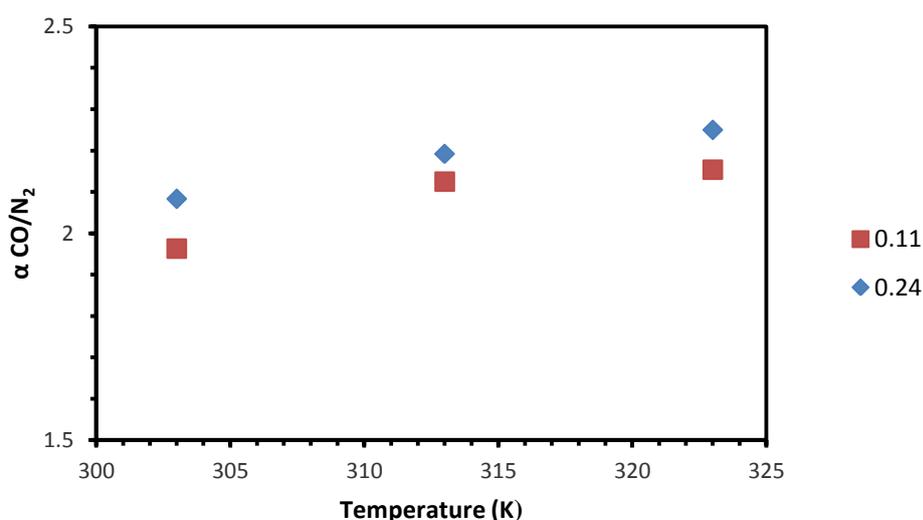


Figure 7. CO/N₂ selectivity behavior with temperature and copper salt concentration comparison between [CuSCN] / [EMIM][SCN] molar ratio=0.11 and 0.24 with pure feed gas.

Mixed gas permeation tests were also performed to obtain mixed-gas CO/N₂ selectivity and permeabilities and to compare them with the above pure gas results. The experiments were performed with both copper (I) - containing SILMs at 0.11 and 0.24 molar ratios at the same temperature and pressure conditions than the above pure gas permeation tests. The mixture gas stream consisted of 50/50 vol% of CO/N₂. Permeability coefficient results are collected in **Table 9**.

Table 9. Gas permeability results through the copper (I)- containing SILMs as a function of temperature and copper concentration at 1.3 bar with mixed feed gas

CuSCN/[EMIM][SCN]	Temperature(K)	P (Barrers)	
		N ₂	CO
0.11	303	4.3	5.5
	313	5.1	6.7
	323	5.8	8.9
0.24	303	4.2	5.2
	313	4.4	5.7
	323	5.8	8.8

Figure 8 shows the comparison between CO/N₂ selectivity obtained with pure feed gas and the selectivity obtained with mixed feed gas permeation results of copper(I)-containing SILM at 0.11 molar ratio, previously presented at different temperatures from 303 to 323K.

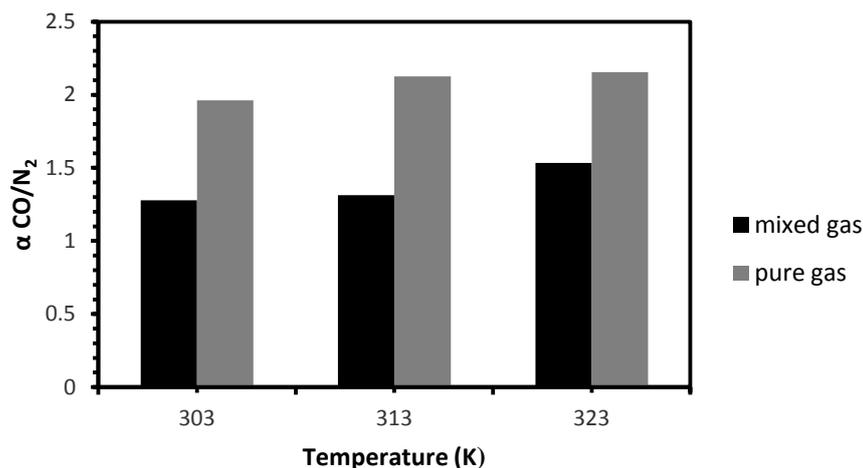


Figure 8. CO/N₂ selectivity comparison between mixed feed gas and pure feed gas at [CuSCN]/ [EMIM] [SCN] molar ratio=0.11

It can be seen that the CO/N₂ selectivity decreases significantly when mixed feed gas is used in gas permeation tests. This effect can be explained by an increase of N₂ permeability while CO permeability was kept constant irrespective of the type of feed gas employed; this effect was also observed by Zarca et al. in a different type of copper(I)-containing SILMs [3].

Figure 9 also shows the same comparison between CO/N₂ selectivity obtained with pure feed gas and the selectivity obtained with mixed feed gas permeation results of copper(I)-containing SILM at 0.24 molar ratio.

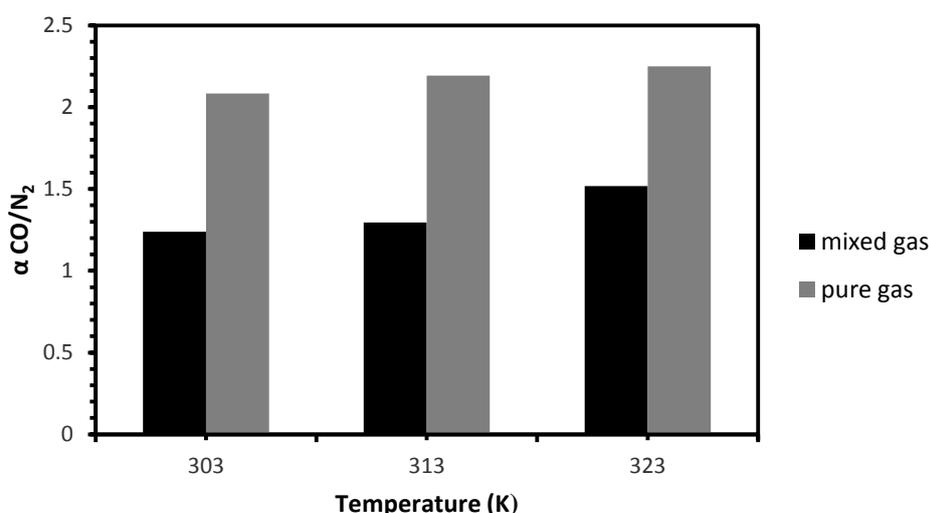


Figure 9. CO/N₂ selectivity comparison between mixed feed gas and pure feed gas at [CuSCN]/[EMIM][SCN] molar ratio=0.24

As it is noticeable, the behavior of CO/N₂ selectivity is the same when the concentration of copper salt was increased. Thus, the content of copper (I) do not promote the decreasing of the difference between pure and mixed feed gas permeation results.

All these detailed results are limited by the need of a driving force increase to achieve higher selectivities and permeabilities. Stability problems were attempted to be solved with the other type of membrane permeation results described below.

5.3 Gas permeation through [EMIM] [SCN] – CILPMs

First of all, only PEBAX polymer membrane gas permeation test was performed in order to know the baseline conditions without ionic liquid influence.

Permeate fluxes and permeability coefficients obtained for all measured gases and several feed pressures are listed in **Table 10**.

Table 10. Permeability coefficient, permeate fluxes PEBAX membrane gas permeations results

ΔP (bar)	P (barrers)			Flux $\cdot 10^5$ (mol/m ² ·s)		
	1.3	2	3	1.3	2	3
N₂	3.9	3.7	3.7	0.37	0.54	0.8
H₂	20.4	20.3	20	1.93	2.96	4.36
CO	2.3	2.3	2.3	0.5	0.34	0.21
CO₂	101.8	104.6	106.3	9.64	15.24	23.21

As it is shown in **Table 11**, which collects different gas selectivity values, CO/N₂ selectivity is not favored with pure PEBAX membrane. In terms of selectivity improvement, only CO₂/N₂ selectivity presents an increase of selectivity as pressure is increased. This effect can be explained by high CO₂ solubility values through the membrane.

Table 11. Gas selectivity results through PEBAX Membrane from 1.3 to 3 bar.

ΔP (bar)	$\alpha(\text{CO}/\text{N}_2)$	$\alpha(\text{H}_2/\text{N}_2)$	$\alpha(\text{H}_2/\text{CO})$	$\alpha(\text{CO}_2/\text{N}_2)$
1.3	0.5	5.2	8.9	26.1
2	0.6	5.5	8.8	28.2
3	0.6	5.4	8.7	28.7

Figure 10 shows the permeate molar fluxes of CO and N₂ pure gases through the PEBAX membrane, which display a linear pattern, i.e, the flux linearly increases as the partial pressure gradient is increased from 1.3 bar to 3 bar at 303 K, which is the driving force of the separation.

This behavior is explained according to the solution-diffusion model, which is based on the fact that although the fluids on either side of a membrane may be at different pressures and concentrations, within a perfect solution-diffusion membrane only a concentration gradient exists. Therefore, the permeability coefficient of each gas remains constant.

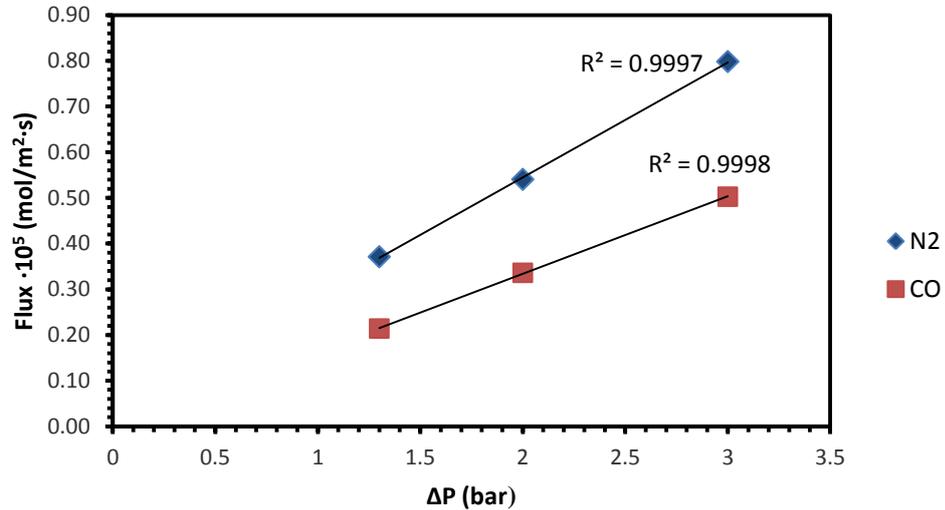


Figure 10. Gas permeate flux vs. Partial pressure gradient of CO and N₂ through PEBAX membrane at 303 K

Figure 10 only shows CO and N₂ results due to their similarity in comparison with H₂ and CO₂ ones, which present a great difference but also a linear behavior.

Then, IL-based composite ionic liquid polymer membranes were tested at different polymer/IL ratios.

[EMIM] [SCN]-CILPM at 80/20 polymer/ IL ratio gas permeation experiments were performed obtaining the results listed in Table 12. According to this information, it can be seen that the expected enhanced membrane properties were reached since the permeability coefficients are much higher.

Table 12. Permeability coefficient, permeate fluxes [EMIM][SCN]-PEBAX CILPM (80/20) gas permeation results

	P (barrers)			Flux · 10 ⁵ (mol/m ² ·s)		
ΔP (bar)	1.3	2	3	1.3	2	3
N ₂	8	7.2	6.6	0.79	1.07	1.65
H ₂	36.1	36.7	35.4	3.49	5.46	7.9
CO	11.3	11.5	11.1	1.11	1.71	2.47
CO ₂	170	171	153.4	16.45	25.51	38.54

As can be noticed in **Table 13**, which collects gas selectivity results through the [EMIM] [SCN]-CILPM at 80/20 polymer/ IL ratio, CO/N₂ selectivity is increased by adding the IL. However, the rest of selectivity values are decreased in comparison with PEBAX membrane selectivity results. This is because CO permeation is favored.

Table 13. Gas selectivity results through [EMIM] [SCN]-PEBAX CILPM (80/20) from 1.3 to 3 bar.

ΔP (bar)	$\alpha(\text{CO}/\text{N}_2)$	$\alpha(\text{H}_2/\text{N}_2)$	$\alpha(\text{H}_2/\text{CO})$	$\alpha(\text{CO}_2/\text{N}_2)$
1.3	1.4	4.5	3.2	21.2
2	1.6	5.1	3.2	23.7
3	1.7	5.4	3.2	23.2

The permeate molar fluxes of CO and N₂ pure gases through the [EMIM] [SCN]-CILPM at 80/20 polymer/ IL ratio, plotted in **Figure 11**, present also the linear behavior as the driving force is increased. All R-squared values are above 99 %.

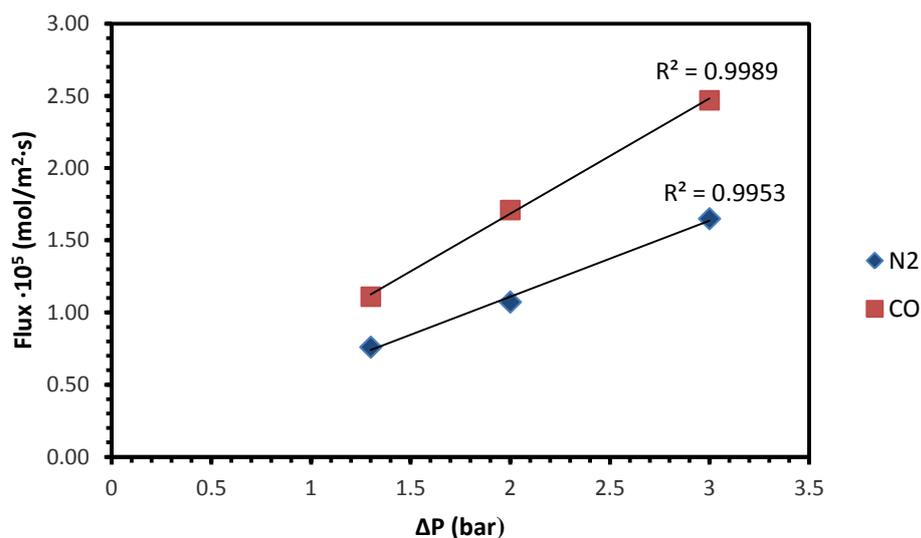


Figure 11. Gas permeate flux vs. Partial pressure gradient of CO and N₂ through [EMIM][SCN]-PEBAX CILPM (80/20) at 303 K

Table 14 shows permeability coefficients of each measured pure gas through a [EMIM][SCN]-CILPM at 70/30 polymer/IL ratio. As it was expected, permeabilities are increased due to a higher content of ionic liquid in the CILPM.

Table 14. Permeability coefficient, permeate fluxes [EMIM][SCN]-PEBAX CILPM (70/30) gas permeation results

ΔP (bar)	P (barrers)			Flux · 10 ⁵ (mol/m ² ·s)		
	1.3	2	3	1.3	2	3
N ₂	8.7	7.6	6.9	0.53	0.72	0.98
H ₂	38.1	36.4	34.5	1.52	2.23	3.16
CO	14.2	14.3	14.0	0.87	1.35	1.98
CO ₂	218.8	225.6	227.3	13.42	21.29	32.17

Table 15 shows gas selectivity results through the [EMIM][SCN]-CILPM at 80/20 polymer/IL ratio. As can be seen, CO/N₂ selectivity increases as the content of ionic liquid is increased. In the same way than in the above explained membrane, CO permeation is favored. However, CO₂/N₂ selectivity is also increased in this case. So that, CO₂ permeation is also favored by adding the target ionic liquid.

Table 15. Gas selectivity results through [EMIM] [SCN] - PEBAX CILPM (70/30) from 1.3 to 3 bar.

ΔP (bar)	$\alpha(\text{CO}/\text{N}_2)$	$\alpha(\text{H}_2/\text{N}_2)$	$\alpha(\text{H}_2/\text{CO})$	$\alpha(\text{CO}_2/\text{N}_2)$
1.3	1.6	4.4	2.7	25.1
2	1.9	4.8	2.5	29.7
3	2.0	5	2.4	32.9

Figure 12 shows the molar fluxes of CO and N₂ pure gases through the [EMIM] [SCN]-CILPM at 70/30 polymer/ IL ratio. The linear pattern is also appreciated as the partial pressure gradient is increased from 1.3 bar to 3 bar at 303 K.

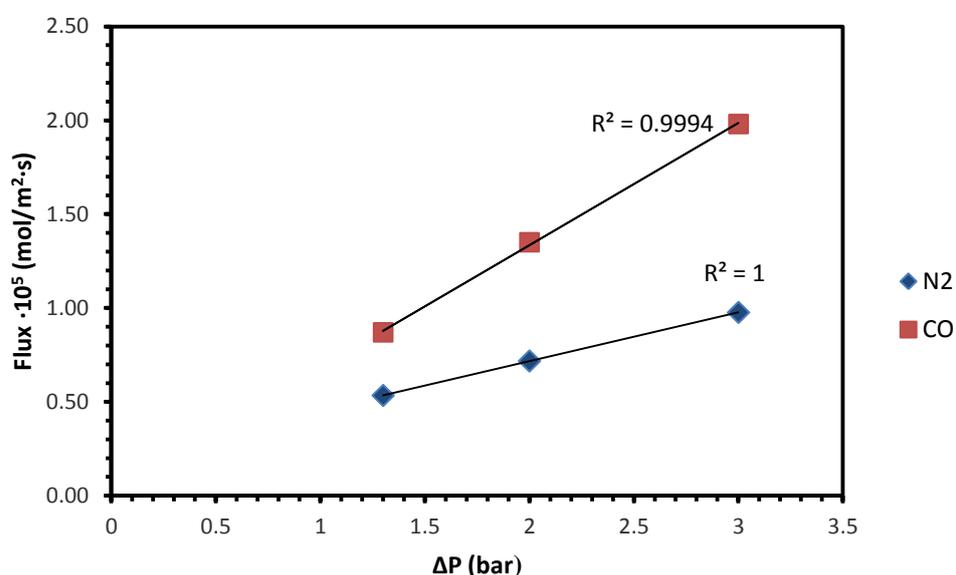


Figure 12. Gas permeate flux vs. Partial pressure gradient of CO and N₂ through [EMIM][SCN]-PEBAX CILPM (70/30) at 303 K

CO permeation test were also performed up to 7 bars in order to assess whether permeability remains constant or is affected by membrane plasticization phenomena. The permeability can be calculated with the slope plotted in Figure 13, being 71 μm the thickness of the membrane.

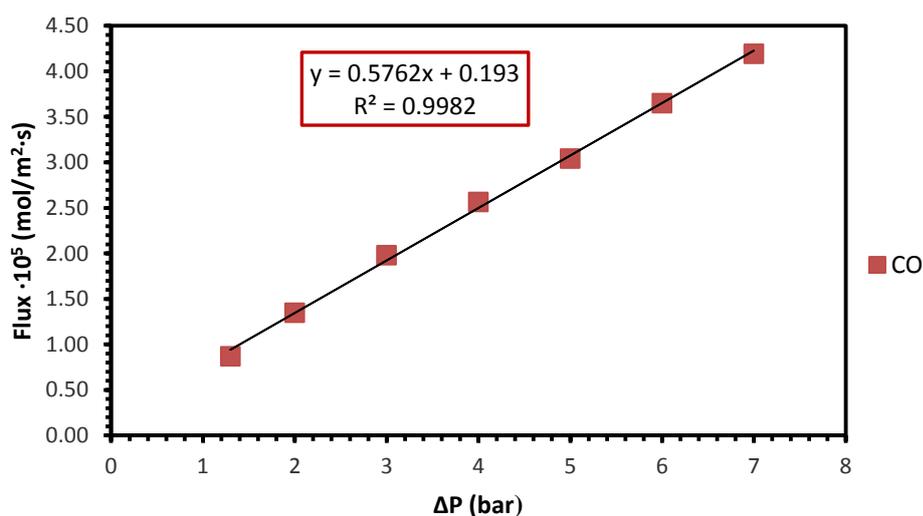


Figure 13. Gas permeate molar flux vs. Partial pressure gradient of CO through [EMIM][SCN]-PEBAX CILPM (70/30) at 303 K.

Permeability value according to this approach is equal to 13.7 Barrers. Thus, permeability also remains constant at high driving force values and plasticization is not observed with CO permeation.

In order to enhance CO permeation results through CILPMs, Cuprous Thiocyanate (CuSCN) copper (I) salt was added. For that purpose, CILPMs were tested changing the ratios polymer/ ionic liquid and ionic liquid/copper (I) salt. It was also tested by changing the material of the flat surface (plate) where the casting took place. Casting operation conditions also varied depending on the type of solvent used. It should be noticed that finding an appropriate solvent to dissolve the selected polymer, IL and copper salt, represents a huge challenge.

Test conditions and membrane quality results are listed in **Table 16**.

Table 16. CILPMs test conditions and quality results

Ratio Polymer/IL	Polymer	Ratio IL/CuSCN	Solvent	Operation conditions	Plate	Mechanical stability	Homogeneity
100/0	PVDF-HFP	100/0	THF	T=25°C P= 700 mbar	Glass	Yes	Homogeneous
80/20	PVDF-HFP	100/0	THF	T=25°C P= 700 mbar	Glass	Yes	Phase dispersion
100/0	PVDF-HFP	100/0	Acetone	Room conditions	Glass	Yes	Homogeneous
90/10	PVDF-HFP	100/0	Acetone	Room conditions	Glass	Yes	Phase dispersion

80/20	PVDF-HFP	100/0	Acetone	Room conditions	Glass	Yes	Phase dispersion
60/40	PVDF-HFP	100/0	Acetone	Room conditions	Glass	Yes	Phase dispersion
40/60	PVDF-HFP	100/0	Acetone	Room conditions	Glass	Yes	Loss of ionic liquid
90/10	PVDF-HFP	100/0	Acetone	Room conditions	Teflon	Yes	Homogeneous
80/20	PVDF-HFP	100/0	Acetone	Room conditions	Teflon	Yes	Homogeneous
70/30	PVDF-HFP	100/0	Acetone	Room conditions	Teflon	Yes	Homogeneous
60/40	PVDF-HFP	100/0	Acetone	Room conditions	Teflon	Yes	Loss of ionic liquid
80/20	PVDF-HFP	80/20	Acetone	Room conditions	Teflon	Yes	Phase dispersion
70/30	PVDF-HFP	80/20	Acetone	Room conditions	Teflon	Yes	Non homogeneous
100/0	PAN	100/0	NMP	T=40°C P= 100 mbar	Glass	No	Crystallized
90/10	PAN	100/0	NMP	T=40°C P= 100 mbar	Glass	No	Crystallized
60/40	PAN	100/0	NMP	T=40°C P= 100 mbar	Glass	No	Gelatinous
80/20	PAN	100/0	NMP	T= 40°C P= 100 mbar	Glass	Yes	Phase dispersion
100/0	PEBAX	100/0	n-butanol	T=45°C P= 300 mbar	Teflon	Yes	Homogeneous
80/20	PEBAX	100/0	n-butanol	T=45°C P= 300 mbar	Glass	Yes	Homogeneous
80/20	PEBAX	80/20	n-butanol	T=45°C P= 300 mbar	Glass	Yes	Cu SCN not dissolved
80/20	PEBAX	80/20	THF	T= 25 °C P=700 mbar	Glass	Yes	Phase dispersion
70/30	PEBAX	100/0	n-butanol	T= 45 °C P=300 mbar	Glass	Yes	Loss of ionic liquid
60/40	PEBAX	100/0	n-butanol	T= 45 °C P=300 mbar	Glass	Yes	Loss of ionic liquid
80/20	PEBAX	90/10	n-butanol/THF	T= 45 °C P=600 mbar	Glass	Yes	Partially homogeneous

According to the information collected in **Table 12**, some tests results were obtained. Regarding PVDF-HFP polymer, it is soluble either with Tetrahydrofuran or with Acetone.

However, when the target ionic liquid is added, the casting conditions are limited to take place in a Teflon plate to be homogeneous. When the casting took place on a glass plate, the membranes developed phase dispersion.

The membranes were homogeneous on a Teflon plate until the ratio 60 /40 when the loss of the ionic liquid inside the membrane was appreciated. Furthermore, when copper thiocyanate was added to the solution, membranes developed phase dispersion with both material plates.

PAN polymer presented difficulties to achieve mechanical stability when the casting was performed. Thus, different polymer/IL ratios were tested. When the ratio is high, the membrane tended to be crystallized and partially broken. However, when the ratio is low, the membrane became gelatinous being impossible its handling. At the ratio 80/20, good mechanical stability was achieved. However, the membrane was not homogeneous.

Finally, PEBAX polymer and the ionic liquid were dissolved with n-butanol with high-quality membrane results. Therefore, PEBAX membranes were chosen to perform gas permeation tests until 70/30 ratio, which is the highest ratio reached with high quality appearance.

Nevertheless, copper thiocyanate could not be dissolved in n-butanol. Therefore, the solution of PEBAX in THF was tested, which is compatible with the salt, but the polymer is just partially dissolved.

The last attempt was a solvent mixture of n-butanol and THF obtaining partially fully polymer solubility and partially copper salt solubilization. The membrane obtained, with an 80/20 polymer/IL ratio and 90/10 IL/copper (I) ratio, was measured with gas permeation processes at 303 K obtaining, as it is shown in **Table 17**, lower values of permeability coefficients in comparison with the above pure IL-based CILPMs at the same ratio polymer/IL. However, the ideal selectivity CO/N₂ has higher value.

Table 17. Gas permeability and molar flux results through copper (I) thiocyanate-CILPM with 80/20 PEBAX/[EMIM][SCN] and 90/10 [CuSCN]/ [EMIM][SCN] at 303K

	P (barrers)			Flux ·10 ⁵ (mol/m ² ·/s)		
ΔP (bar)	1.3	2	3	1.3	2	3
N ₂	5.1	4.9	4.8	0.44	0.66	0.97
H ₂	27.6	27.5	26.7	2.4	3.68	5.36
CO	10.6	10.8	9.7	0.92	1.45	2.17

Table 18 collects different gas selectivity values from 1.3 to 3 bars as the driving force at 303 K.

Table 18. Gas selectivity results through copper (I) thiocyanate-CILPM with 80/20 PEBAX/ [EMIM][SCN] and 90/10 [CuSCN]/ [EMIM][SCN] at 303 K

ΔP (bar)	$\alpha(\text{CO}/\text{N}_2)$	$\alpha(\text{H}_2/\text{N}_2)$	$\alpha(\text{H}_2/\text{CO})$
1.3	2.0	5.4	2.6
2	2.2	5.6	2.5
3	2.0	5.5	2.7

In order to assure that the increase in selectivity involved an enhancement of CILPMs gas separation properties, gas permeation results were repeated increasing the temperature from 303 K to 313 K. **Table 19** collects the copper (I) thiocyanate-CILPM gas permeation results at 313 K.

Table 19. Gas permeability and molar flux results through copper (I) thiocyanate-CILPM with 80/20 PEBAX/[EMIM][SCN] and 90/10 [CuSCN]/ [EMIM][SCN] at 313K

	P (barrers)			Flux ·10 ⁵ (mol/m ² ·/s)		
ΔP (bar)	1.3	2	3	1.3	2	3
N ₂	7	6.8	7.3	0.61	0.91	1.33
H ₂	38.1	38.6	37.8	2.99	4.65	6.83
CO	15.1	15.2	15.3	1.32	2.04	2.77

Table 20 also collects different gas selectivity values from 1.3 to 3 bars as the driving force at 313 K.

Table 20. Gas selectivity results through copper (I) thiocyanate-CILPM with 80/20 PEBAX/[EMIM][SCN] and 90/10 [CuSCN]/ [EMIM][SCN] at 313K

ΔP (bar)	$\alpha(\text{CO}/\text{N}_2)$	$\alpha(\text{H}_2/\text{N}_2)$	$\alpha(\text{H}_2/\text{CO})$
1.3	2.1	5.4	2.5
2	2.2	5.6	2.5
3	2.1	5.2	2.4

As can be seen with the comparison between **Table 18** and **Table 20**, the increase of the selectivity value is practically negligible. Thus, CO/N₂ selectivity is not promoted by an increase in temperature. This effect can be explained as a decrease of CO solubility with the reactive salt. It can be noticed that H₂/N₂ and H₂/CO selectivities were not increased either.

For all these reasons, in contrast with the above reported SILMs, copper incorporation in the CILPMs with the target ionic liquid of this work could not be practically considered as a way to further enhanced membrane separation properties.

6. Conclusions and future work

In this work, [EMIM] [SCN]-SILMs and [EMIM] [SCN]-CILPMs were performed and tested obtaining the following conclusions:

- Pure [EMIM] [SCN]-SILMs reached low CO and N₂ permeability, being 3.8 and 5.4 barrers respectively; and CO/N₂ and H₂/N₂ selectivity with a value of 1.4 and 3.2 at 303 K respectively. The activation energy of permeation of N₂, CO and H₂ were also calculated, being these values 5.8, 6.0 and 6.3 kJ/mol, respectively.
- Copper (I)-containing SILMs shown a significant improvement for gases separation due to higher CO/N₂ selectivity values as copper content increased, being 1.96 and 2.1, for 0.11 and 0.24 copper molar ratio respectively at 303 K. Also, higher selectivities were appreciated as temperature increased.
- Selectivity values were higher employing pure gases than mixed gases as the feed resource.

- It was also appreciated a decrease of N₂ and H₂ permeability coefficients while CO permeability slightly increased. This effect can be explained by a reverse effect in which CuSCN addition can restrict diffusivity and decrease some gas permeability, and because CO permeation through the membrane is favored.
- Gas permeabilities through CILPMs presented a linear behavior as driving force was increased according to solution-diffusion model and membrane plasticization was not observed. As the ionic liquid content increased, gas permeabilities and CO/N₂ selectivity increased too, obtaining a value of CO and N₂ permeability of 11.3 and 7.2 barrers respectively, and a selectivity value of 1.57 for 80/20 CILPMs. For 70/30 CILPMs, CO and N₂ permeability values were 14.2 and 7.7 respectively with a selectivity value of 1.84.
- Copper (I) containing-CILPMs were obtained dissolving the target ionic liquid, PEBAX polymer and copper (I) salt in a mixture of n-butanol and THF achieving partially-fully solubilisation.
- Copper (I) containing - PEBAX CILPMs achieved lower values of permeability and slightly higher CO/N₂ selectivity values than the IL-based CILPMs. However, CO/N₂ selectivity values did not increase with temperature. This temperature effect can be explained by a non proper copper solution in the membrane. This problem could be analyzed in future works characterizing the membrane with one of the characterization methods suggested in this work in order to determine components distribution through the membrane. It could be a way of finding a solution to consider the copper salt adding as an enhanced CILPM property.

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