

Application of supported ionic liquid membranes in the purification of bio-based molecules using
pervaporation
(Methanol and dimethyl carbonate separation)

Dissertation presented by
Cristhian MOLINA FERNANDEZ

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Supervisor(s)
Patricia LUIS ALCONERO

Readers(s)
Damien DEBECKER, Patrick GERIN

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Abstract

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Application of supported ionic liquid membranes in the purification of bio-based molecules using pervaporation: Methanol and dimethyl carbonate separation

by Cristhian Molina Fernández

The use of supported ionic liquid membranes in organophilic separation is an unexplored field. For this reason this work aim to test the separation performance of methanol and dimethyl carbonate mixtures by supported ionic liquids membranes. Immobilisation tests, pervaporation experiments with pure methanol and dimethyl carbonate at different temperatures and pervaporation experiments with different concentrations of the binary mixture were carried out. Using the results of these experiments and different solution parameters, interaction between solute and ionic liquid molecules was elucidated. [OMIm][NTf₂] and [OMPyrr][NTf₂] immobilised in PAN membranes provided a very selective separation of DMC. Coupling effects hindered methanol permeance. Some supported ionic liquid membranes presented sudden changes in their permeance. These changes are attributed to atmospheric water absorption and to chemical reactions in the membrane as a consequence of solute, ionic liquid and membrane interactions.

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List of Abbreviations

GL	Glycerol
GC	Glycerol Carbonate
DMC	Dimethyl Carbonate
MEOH	Methanol
EC	Ethylene Carbonate
LM	Liquid Membrane
SLM	Supported Liquid Membrane
IL	Ionic Liquid
SILM	Supported Ionic Liquid Membrane
PAN	Polyacrylonitrile
PP	Polypropylene

Chapter 1

Literature Study

1.1 Biodiesel Glycerol Problem

The increment in environmental awareness, depletion of fossil fuel resources and the increase in their cost are driving the change of our society, whose energy demand is continuously increasing, from a fossil feed-stock to a renewable feed-stock, the so called *biofuels* [1]. Biofuels are produced from bio-natural resources such as plants, animal fats or biomass and they represent a good candidate to replace fossil fuels due to their lower environmental impact, possibility of implementation in industrialised and developing countries, foreign exchange savings and greater energy security [2]. Biofuels can be found in gas, liquid, or solid form and they can be classified into two groups: primary biofuels, those that are generated directly from natural materials (burning wood or dry animal waste) and secondary biofuels, those that are indirectly generated from natural materials. There are three generations of secondary biofuels that are summarised in Table 1.1 [3].

Biofuels			
Primary	Secondary		
	First generation	Second generation	Third generation
Firewood, wood chips, pellets, animal waste, forest and crop residues, landfill gas	Bioethanol or butanol by fermentation of starch (from wheat, barley, corn, potato) or sugars (from sugar cane and sugarbeet) Biodiesel by transesterification of oil crops (rapeseed, soybeans, sunflower, palm, coconut, used cooking oil, and animal fats.)	Bioethanol and biodiesel produced from conventional technologies but based on novel starch, oil and sugar crops such as jatropha, cassava or miscanthus Bioethanol, biobutanol, syndiesel produced from lignocellulosic materials (e.g. straw, wood and grass)	Biodiesel from microalgae Bioethanol from microalgae and seaweeds Hydrogen from green microalgae and microbes

TABLE 1.1: Classification of biofuels [3].

Among secondary biofuels, *biodiesel* is one of the most important nowadays. It is a liquid biofuel generally produced from vegetable oils and animal fats by different chemical processes. One of the most important processes is the transesterification reaction. This reaction is sketched in Figure 1.1. In this reaction a molecule of triglyceride, coming from different raw materials, will react with an alcohol, typically methanol because it is the cheapest, to produce an alkyl ester (methyl ester) and glycerol. The reaction is generally carried out in

presence of alkaline catalyst (NaOH or KOH)[4]. However, acid catalyst and enzymes may be used as well [5] [6].

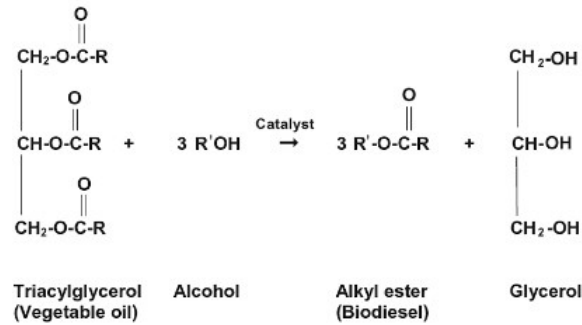


FIGURE 1.1: The transesterification reaction. R is a mixture of various fatty acid chains. The alcohol used for producing biodiesel is usually methanol [7].

The long and unbranched fatty acid chains provide a suitable cetane number (CN) to biodiesel. CN describes the ignition quality of diesel and it is analogous to the octane number for gasoline. Furthermore, biodiesel has a heat content near of 90 % of conventional diesel and similar viscosity and it is non-toxic, renewable and biodegradable [7]. For this, biodiesel is a suitable substitute of conventional diesel and its production (as other biofuels) has undergone a large increment in the past decade as can be seen in Figure 1.2.

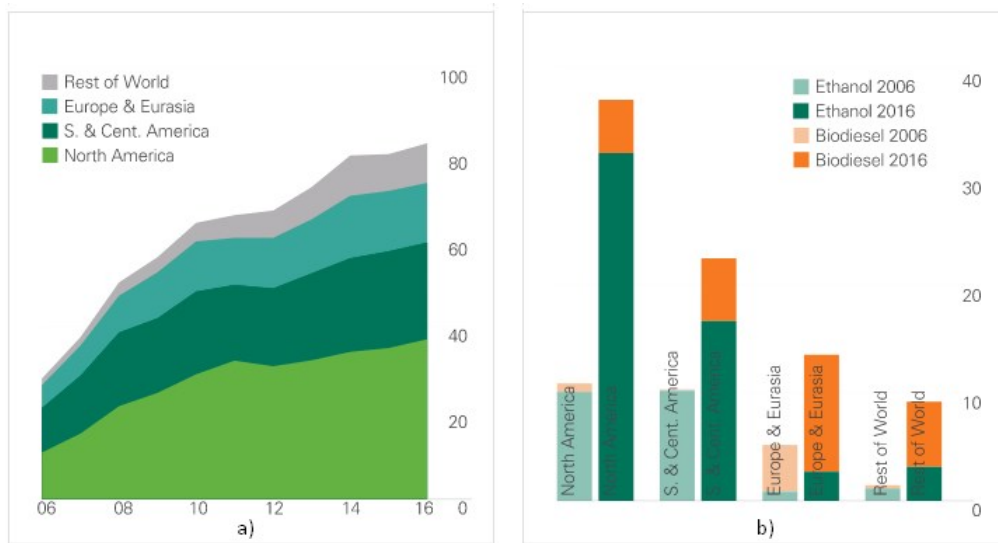


FIGURE 1.2: a) World biofuels production by region (million tonnes oil equivalent), b) World biofuels production by type (million tonnes oil equivalent) [8].

Along with this large production of biodiesel, there is a large amount of *Glycerol* (GL) that is produced as by-product. Per every 100 kg of biodiesel produced by transesterification, 10 kg of crude GL is produced [9]. Crude GL is the GL rich phase produced in the transesterification reaction, once separated from the biodiesel phase [10], see Figure 1.3. Nowadays, biodiesel production is the main source of GL. For that reason, both markets are very dependent on each other and the increase of biodiesel production is creating a surplus of GL in the

market and a drop in its price [11]. Furthermore, crude GL contains impurities such as catalyst, water, soap and esters being the GL content of crude GL about 30-60 % in weight [12]. In consequence, crude GL has to be purified before being used as feedstock in the chemical industry which increases production cost. There are different methods and hybrid methods that can be applied in order to purify crude GL such as distillation, ion-exchange, adsorption, extraction, filtration or decantation. The most common way is distillation combined with ion exchange removal of salts and activated carbon adsorption [13].

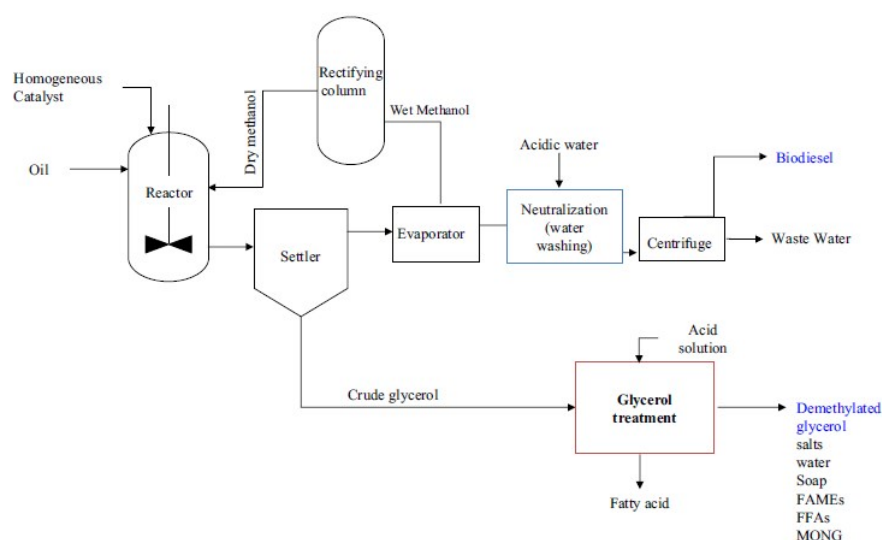


FIGURE 1.3: Conventional homogeneous biodiesel production process flow diagram [14].

Once crude GL has been purified up to 99.5 - 99.7 % [15] it can be used as feedstock in a large number of applications. Figure 1.4 shows the main fields of application of GL.

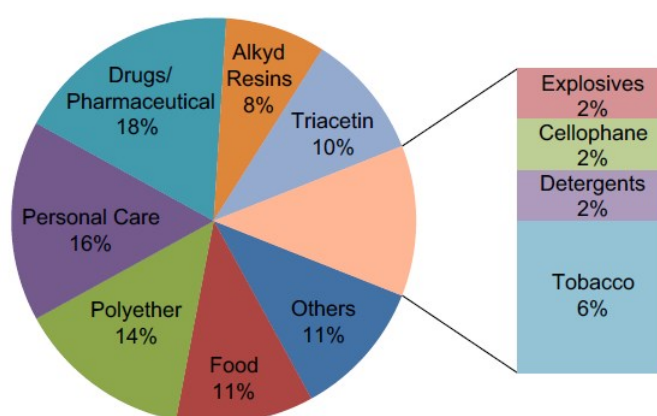


FIGURE 1.4: Glycerol industrial applications [16].

Several studies have been carried out in order to find new applications to elevate the market value of the GL produced in biodiesel industry. But, for the moment, only hydrogen gas, polyglycerols, epichlorodrin and polyol polyurethane foams can be produced

directly from crude GL [14]. In Figure 1.5 are showed the different valuable derivatives that could be produced from GL.

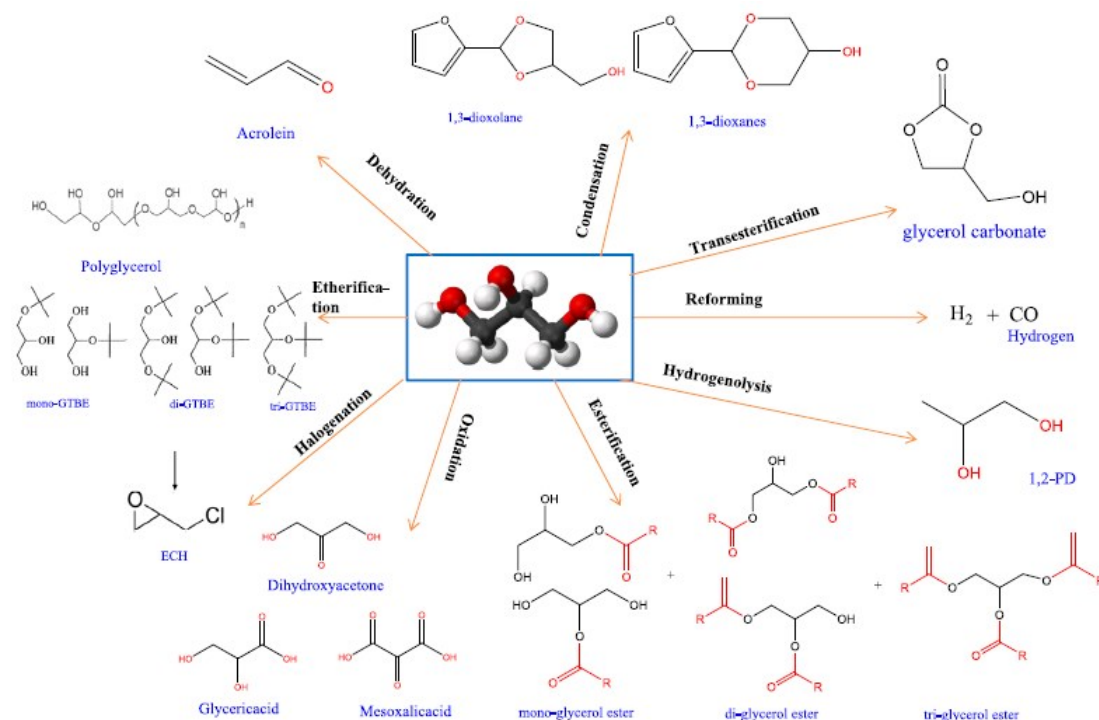


FIGURE 1.5: Possible glycerol derivatives via different pathways [14].

The present study is going to be focused on one of these derivatives, the glycerol carbonate molecule. More precisely the performance of a new technique based on supported liquid membranes for the purification of glycerol carbonate is going to be studied.

1.2 Glycerol carbonate a green chemical

In this section, the characteristics of glycerol carbonate are discussed as well as the different ways to produce it and the main alternatives of recovery it from the reaction mixture.

1.2.1 Introduction

Glycerol Carbonate (GC) is a glycerol ester whose structure is depicted in Figure 1.6. It is a stable and colourless viscous liquid with low toxicity, high boiling point, not flammable, moisturising properties and biodegradability. Due to its functional groups it can be used as solvent for organic and inorganic compounds. In consequence, it can be used to make solutions of plastics, resins, cosmetics, paints, battery electrolyte, medical goods, etc [17] [18] [19] [20].

Also, GC molecule contains four reactive sites (the three carbons of the ring and the carbon connected to the hydroxyl group) that react with different compounds such as alcohols, carboxylic acids and phenols. That creates a large number of possible reactions and products. For that reason, along with its renewable character (produced from natural resources), GC could be used as a substitute of base chemicals derived from petro-chemical industry in chemical synthesis [21][22]. Potential uses of GC are showed in Figure 1.6.

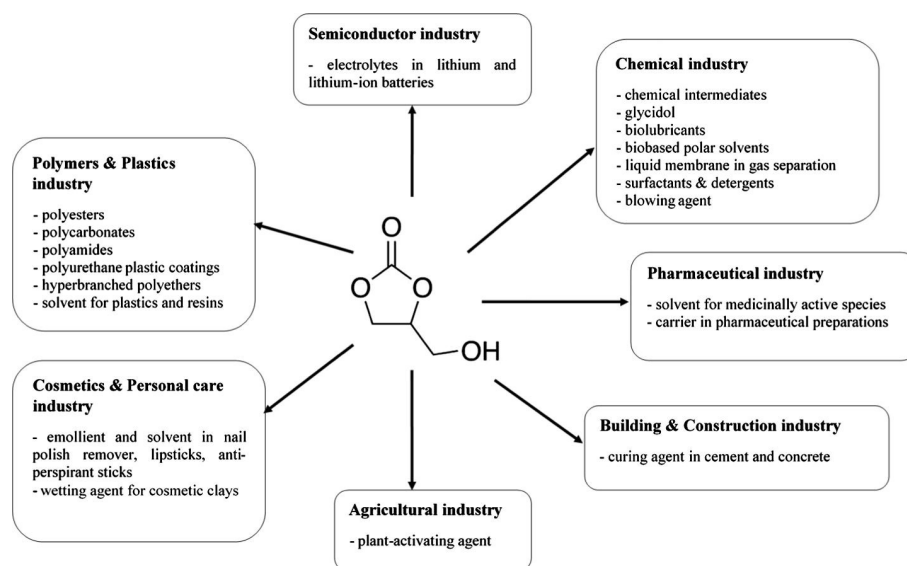


FIGURE 1.6: The potential uses of glycerol carbonate in various industries [23].

This chemical has received special attention in recent years as it is a possible solution to the GL problem. However, despite it is a highly valued chemical, it has not a large range of applications due to its high cost [23].

1.2.2 Glycerol carbonate synthesis methods

In order to achieve the feasibility of industrial applications, GC production process from GL has to satisfied some requirements [22] such as:

- Fast reaction with high conversion and selectivity towards the desired product.
- Use a cheap, recoverable and recyclable catalyst.
- Easy separation and purification of the final product.
- Safe and environmentally friendly process.

Only those processes that fulfilled these requirements will be described here. They can be divided in two groups depending on whether the synthesis is direct or indirect.

Direct synthesis

GC can be synthesised by direct reaction of GL with CO₂ through the following reaction:

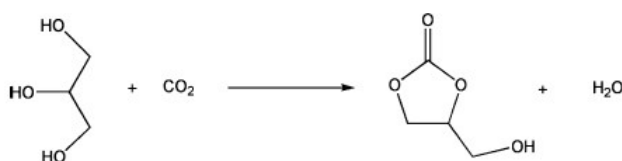


FIGURE 1.7: Direct synthesis of glycerol carbonate [22].

At first sight, this seems to be the best process since GC is produced from two available and cheap raw materials that in this context can be considered as wastes. In addition, this would provide a new use for CO₂ which is a green house effect gas. However, GL conversion towards GC has always been below 20% as it has been tested with several catalysts and reacting conditions. Ozoiro et al. [24] investigated metal-impregnated zeolite catalysts. Although working at 180 °C during 3 h and at a high pressure (100 Bar) a maximum poor yield of 5.8% is achieved. Park et al. [25] studied La₂O₂CO₃/ZnO catalysts prepared by two different methods, co-precipitation and ethylene glycol solution combustion. They found a yield of 14.4 and 9.1 % respectively. Finally, Li et al. [26] prepared different catalysts based on Zn–Al–La oxides modified with various halogen anions. A yield of 16 % for the case of catalysts modified with chloride ions is achieved. Due to this low yield, direct production of GC using CO₂ is not industrially feasible. This is due to the high stability of CO₂ molecule which makes this process thermodynamically limited [22][27].

Indirect synthesis

Since direct synthesis is not feasible, several indirect synthesis have been proposed based on more reactive chemicals derived from CO₂ or GL. In what follows, three important indirect synthesis will be explained.

Transesterification reactions between glycerol and dimethyl/ethylene carbonate

By using transesterification reactions, GC can be obtained with a very high yield [23]. Among different chemicals that can be used in transesterification reactions of GL in order to produce GC, *Dimethyl Carbonate* (DMC) and *Ethylene Carbonate* (EC) are the most important ones [22]. These two reactions are showed in Figure 1.8 with typical values of operating conditions.

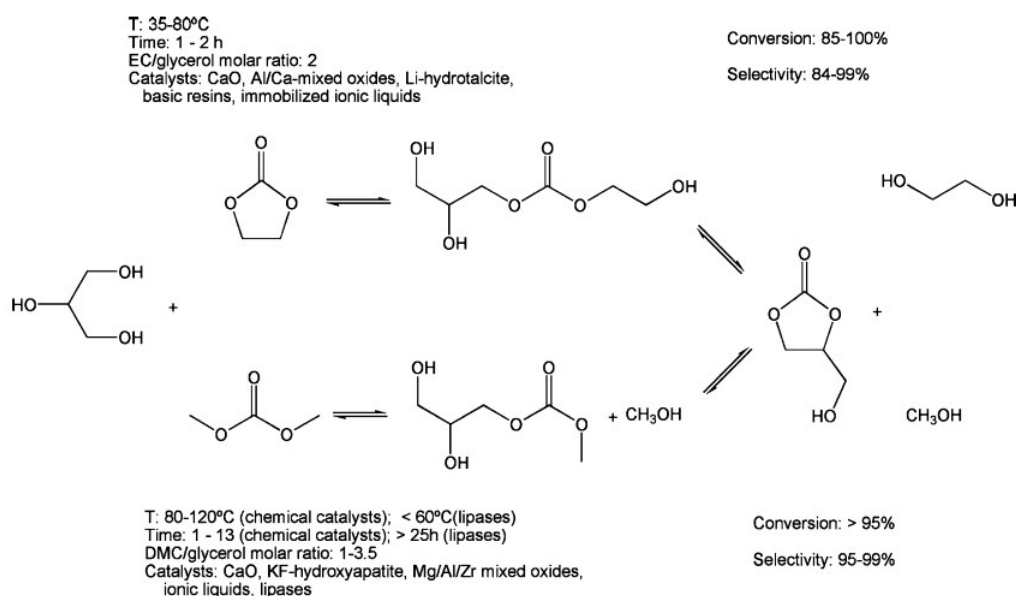


FIGURE 1.8: Transesterification reaction of dimethyl carbonate and ethylene carbonate with glycerol [22].

Comparing the equilibrium constant for both reactants in the transesterification reaction, Li et al. [27] found that equilibrium is favored at low temperature when EC is used and

at high temperature in the case of DMC. That means that a higher temperature is required working with DMC. However, as indicated by Ochoa-Gómez et al.[22], recovery of GC by distillation is more difficult in the case of using EC due to the lower volatility of EC and ethylene glycol compared to DMC and methanol. Furthermore, DMC is environmentally sustainable [28] and EC is considered expensive [29].

DMC can be used as reactant and solvent for the reaction which makes this process free of solvent. Normally DMC is used in molar ratio to GL higher than 1 since this drives the equilibrium towards the products increasing GC yield and eliminates remaining GL from the reaction mixture. This is important because of the high boiling point of GL [30][29].

Several catalysts perform well in these reactions such as metal oxides, ionic liquids, lyase or hydrotalcites. Heterogeneous catalysts are popular since they have high activities and they can be recovered/recycled easily [23]. Basic catalysts have better activities (higher yield and conversion) than acid ones being the most important CaO. CaO would be used as heterogeneous catalyst. However, CaO activity decrease strongly if it is recycled without any pretreatment. Calcination would increase considerably its activity but it consumes a lot of energy so catalyst is not be recycled. But this is not a problem since it is cheap and widely available [30]. Furthermore, CaO wastes are considered to do not cause environmental problems.

Glycerolysis of urea

GC can be also obtained by reaction between GL and urea which is a cheap and available raw material. The reaction is shown in Figure 1.9 along with some typical values of process conditions. It is a two step reversible reaction in which GL is carbamoylated in order to produce glycerol carbamate and this product is carbonylated producing GC. Ammonia is released as byproduct in both steps. That's why it is convenient to work under vacuum to drive the equilibrium to the right [31]. This ammonia rich gas could be used, along with CO₂, to produce urea. High working temperatures are favourable from a thermodynamic point of view [27].

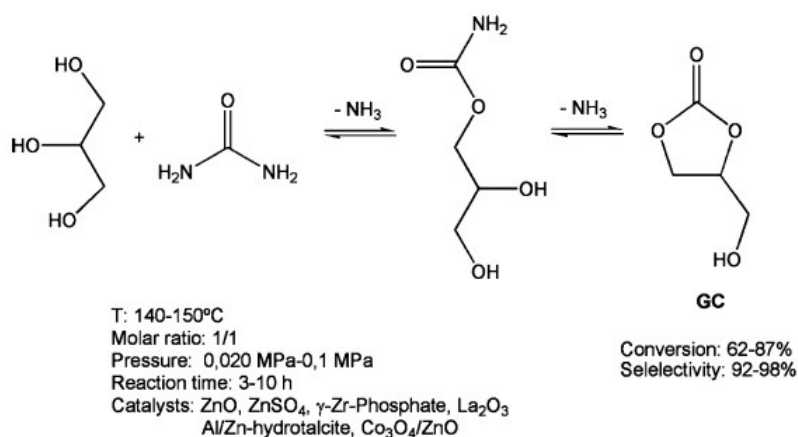


FIGURE 1.9: Synthesis of GC by glycerolysis of urea [22].

This reaction can be performed without catalyst but yields are below 40%. For that reason, different catalysts have been studied achieving conversions up to 83% and high values of selectivity. Initially they were ZnO based homogeneous catalysts due to its acid sites that promotes urea activation. But several solid catalysts have been developed to be able to recover and recycling it such as ZnO supported catalysts [22] [32] [31].

1.2.3 Glycerol Carbonate recovery from reaction medium

In the previous section different ways in which GC can be produced were discussed. However, the scope of this work is centered in studying GC recovery technologies. For that reason, in this subsection, the different separation technologies that have been used to recover GC will be reviewed.

Technology selection will be highly related to the GC synthesis pathway since this will determine the composition of the mixture from where GC has to be extracted.

Direct distillation of reaction mixture is the easiest way to recover GC. This is due to its larger boiling point compared to other unreacted reactants and products that will be present in the reaction mixture (see Table 1.2). However, their values of boiling point are also high which would increase energy consumption during the separation step [30].

TABLE 1.2: Boiling temperatures of compounds under study [33].

Compound	Boiling point at 0.1 MPa [°C]
Glycerol carbonate	354
Glycerol	290
Dimethyl carbonate	90
Methanol	64.5
Ethylene carbonate	261
Ethylene glycol	197
Urea	235

Lertlukkanasuk et al. [34] compared GC recovery produced via glycerolysis of urea using a conventional in "vacuo process". This is made of a reactor from which ammonia is removed by a sweep gas plus a distillation unit with a single reactive distillation unit operating at atmospheric pressure. They performed such comparison using Aspen Plus® and they found that using reactive distillation allows to save 37.1% of energy and increase GL conversion by 29.1%. Unreacted GL and urea are recovered in the distillate and GC in the bottom stream.

For the case of using DMC and GL transesterification, removing methanol (MEOH) during the reaction will shift the equilibrium towards products. This could be done using reactive distillation. However, it is important to take into account that MEOH and DMC form an azeotrope at 30 % in weight of DMC [22]. So, by using conventional distillation both MEOH and DMC will be removed which is not desired since DMC is a reactant. That's why, in order to remove only MEOH, extractive distillation or azeotropic distillation has to be used. Li and Wang [29] studied DMC and GL transesterification reaction with CaO coupled with azeotropic distillation. They found a high yield (98 %) even using 1:1 ratio of DMC to GL thanks to the removal of MEOH. They tested several azeotropic agents and found that benzene was the best. However, as indicated by Wang et al. [35] and Ochoa-Gómez et al. [22], benzene is very toxic and it is recovered in the distillate along with MEOH. Both compounds form an azeotrope which makes difficult benzene regeneration and recovery of MEOH. Wang et al. [35] compared experimental results of GC production via transesterification of GL and DMC with CaO using reactive distillation flowed by extractive distillation. The flowsheet can be seen in Figure 1.10. High values of yield and conversion can be achieved but it requires higher values of DMC to GL ratio in the feed. For example, to achieve 99 % in both the GC conversion and selectivity it is required a ratio of 4. This can be explained by the shift of equilibrium towards the reactants when DMC is removed from the reactive distillation column in the distillate because of the azeotrope. As DMC has to evaporate, higher bottom temperature is required compared to the case analysed by Li and Wang [29]. This excess of DMC also makes more difficult the recovery of GC from the liquid

product. An interesting conclusion of this study is that the best extractive agent that could be used to break the MEOH-DMC azeotrope in the extractive distillation column is toluene but GL (that was less effective) could be used as well.

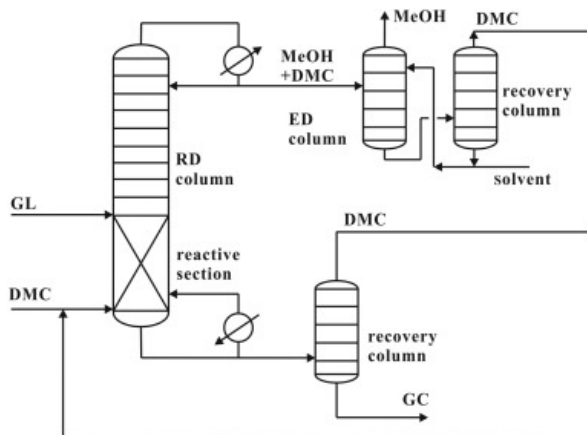


FIGURE 1.10: Synthesis of glycerol carbonate by reactive distillation followed by extractive distillation [35].

Aresta et al. [36] synthesised GC via glycerolysis of urea using different heterogeneous catalysts. They recovered GC from reaction mixture by liquid-liquid extraction. For the solvent that was used, it was required to be selective towards GC, with relatively low boiling point (not too high which will make more difficult its recovery but not too low to limit losses when it is used at reaction temperature) and with different density to improve phase separation. As example, some solvents that fulfil these requirements are acetophenone and acetonitrile. Finally, the solvent is eliminated by distillation or vacuum-distillation and GC is recovered in the bottom. This process is explained in the patent [37] from the same authors. See table 1.3 where different solvents are compared.

TABLE 1.3: Comparison of different solvents for liquid-liquid extraction of glycerol carbonate from a mixture containing glycerol and urea [37].

Solvent	Solubility of Glycerol Carbonate [g/mL]	Solubility of Glycerol [g/mL]	Solubility of Urea [g/mL]	Boiling point at 0.1 MPa [°C]
Acetophenone	>0.5	0.011	<0.004	202
Acetonitrile	>0.5	0.002	<0.001	82
Cyclohexanone	>0.5	0.026	<0.004	155
Diethylketone	>0.5	0.040	<0.004	103
Isophorone				213
Metacrylonitrile	>0.5	0.010	<0.004	92
Methylethylketone	>0.5	0.043	<0.004	79.6
Propionitrile	>0.5	0.016	<0.004	97
Butyronitrile				118
Isobutyronitrile	>0.5	0.01	0.06	107
Pentanenitrile				139-141
Isovaleronitrile	>0.5	0.008	0.058	130

Kim et al. [38] synthesised GC through transesterification of GL and DMC by using immobilised lipase as catalyst. They added molecular sieves of 5 Å in order to remove MEOH from reaction mixture. However, high amounts of these molecular sieves is required (10.5 g/g MEOH).

It could be interesting to point out that MEOH that is recovered could be used as raw material for biodiesel production. This could improve efficiency of biodiesel-glycerol carbonate industrial production plants.

To sum up, classic techniques based on distillation, reactive distillation, vacuum distillation, extractive distillation, azotropic distillation, liquid-liquid extraction and adsorption have been applied to purify and recover GC. However, these techniques required high energy consumption, the use of solvents or large amounts of adsorbents which limits industrial application of large scale GC production. Compared to the other technologies that have been discussed, pervaporation does not require the use of any solvent or adsorbent, it consumes much less energy than classical distillation alone [39] and it is capable to separate azeotropes [40]. These characteristics would make pervaporation a suitable technique to recover GC. Furthermore no previous studies can be found in literature about this topic. For all these reasons, a new procedure of separation based on pervaporation is going to be study in this work.

1.3 Pervaporation systems

Pervaporation is a separation technique based on the use of membranes. In pervaporation a diluted liquid solution, called feed, is put in contact with a asymmetric dense membrane. Since vacuum is applied in the other side of the membrane, components from the feed will dissolve in the membrane by occupying the voids between the polymeric chains and will diffuse through it at different speeds (which causes the selective separation) until they reach to the permeate side. Near of the other face of the membrane these components will volatilise by absorbing sensible heat from the feed because of the lower pressure and they will form a vapor phase called permeate. The liquid solution that is leaving the membrane from the feed side and that is richer in those components that didn't cross the membrane is called retentate [40]. Figure shows 1.11 is showed the scheme of a pervaporation unit.

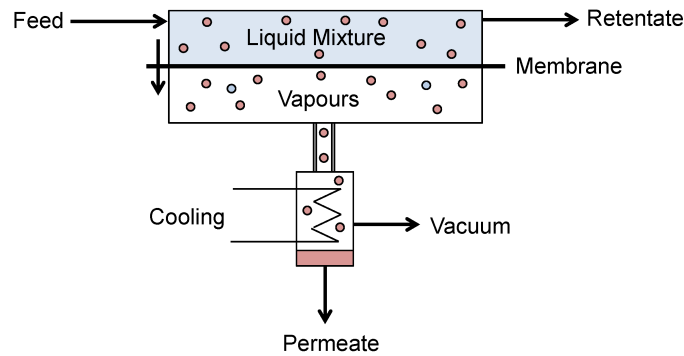


FIGURE 1.11: Conventional pervaporation system [41].

The driven force of pervaporation is the difference of partial vapor pressure of a given specie in both sides of the membrane[41]. The flux of a given component through the membrane can be computed using the solution-diffusion model. Wijmans and Baker [42] proposed the following phenomenological equation:

$$J_i = \frac{P_{M_i}}{l_M} (p_i^{(1)} - p_i^{(2)}) \quad (1.1)$$

Where J_i is the flux of a specie i , P_{M_i} is the permeability of i , l_M is the thickness of the membrane and $p_i^{(1)}$ and $p_i^{(2)}$ are the partial vapor pressures of i at the liquid side and the

vapor side respectively. In pervaporation, the permeability of a given specie is function of the chemical nature of this specie, membrane materials, temperature and concentration of that specie in the membrane. That's why membrane material selection is critical in order to improve membrane performance. For example, in ethanol dehydration, a higher selectivity towards water is required, hydrophilic membrane materials perform better than hydrophobic ones [40].

Regarding to the uses of pervaporation, the main commercialised applications of pervaporation are dehydration of organic solutions and elimination of small amounts of organic components in aqueous solutions such as wastewater [43]. However, more interesting applications are under research. One of these potential applications of pervaporation is organophilic pervaporation. Organophilic pervaporation is the selective separation of components from an organic solution. It is important to make the difference with the currently commercial applications because in this case the components that would be separated in the permeate can be in a large range of concentrations and not only at low concentration in the feed. Also, components that are separated in retentate and permeate have not, in principle, a large difference in hydrophilicity. For this reason, one should not expect to have a good separation simply by using hydrophilic or hydrophobic membranes as in commercial applications. That's why more selective membranes are needed [44]. Among the possible solutions, liquid membranes can provide the required selectivity.

1.4 Liquid membranes

A membrane is generally defined as a physical barrier that separates two phases (feed and permeate side) allowing preferential permeation of certain components [45]. Although a membrane could be seen as a solid barrier, that is not always the case since in the definition is not included the physical state of the barrier. For instance, a liquid that is not mixable with the feed and the permeate but separates both can be considered as a membrane as well. This is called a *Liquid Membrane* (LM)[46].

The use of LMs instead of traditional solid membranes presents some advantages. Firstly, higher flux/permeability can be obtained. This is due to the physical nature of the barrier. As in a solid membrane, certain components will dissolve into the membrane and they will diffuse through it until they reach the permeate side. However, diffusion coefficients in liquids are much higher than in solids [46]. Very selective separations can be also performed thanks to the use of carriers, complexing agents that can be added to the LM. These carriers will react selectively with some molecules of the feed to form molecule-carrier complexes that will diffuse more easily through the membrane. Since this reaction is reversible, these molecules are recovered in the permeate side. This is the so-called facilitated transport [45]. Small amounts of complexing agent are required [46]. See Figure 1.12 for a better understanding of facilitated transport mechanism. Another important fact is that LM systems combine extraction and stripping operations which makes them non-equilibrium limited processes [47].

Different types of configurations are possible for LMs. The main three configurations are sketched in Figure 1.13. In *Bulk Liquid Membranes* (BLM), a thick layer of immiscible liquid, LM, is placed between the feed and the permeate side. It is simple but, due to its high thickness, transport of solute takes longer [46]. *Emulsion Liquid Membranes* (ELM) are formed by emulsification of permeate phase into a continuous LM phase followed by dispersion of this emulsion into the feed solution. This creates small drops of LM in the feed solution. Inside of the drops of LM phase, the permeate phase is dispersed in the form of even smaller drops. This configuration provides the highest interfacial surfaces. However, it is difficult to make

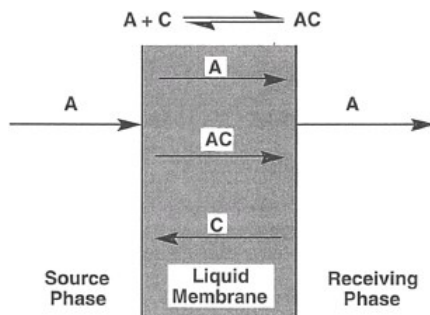


FIGURE 1.12: Scheme of Facilitated Transport mechanism for a solute through a Liquid Membrane. (A is the solute, C is the complexing agent (carrier), and AC is the solute-carrier complex[46].

a stable emulsion that has to withstand agitation but that afterwards has to be easily breakable in order to recover the permeate [46][45]. Finally, in *Supported Liquid Membranes* (SLMs) thickness and amount of solvent is reduced by impregnating the LM into a solid porous support [46]. The Liquid membrane is held in the pores thanks to capillarity [48]. This configuration allows higher rate of transport per unit of volume of liquid membrane [47] than for BLM. An important issue of this configuration compared to the rest is the stability of the membrane [46]. A low stability of a given SLM means that the LM is removed from the pores of the solid supporting porous membrane after relatively low time of operation. This is observed by a quick increase in the flux and a complete loss of selectivity [49]. Low stability of SLM is the main limiting factor for their industrial commercialisation [50]. The stability of a SLM depends on those factors that improve/hinder the formation of emulsions of LM in the feed/permeate side. Among these factors one can find, the stirring speed and transmembrane pressure (working conditions), osmotic pressure and carrier concentration (interaction with feed/permeate) and the hydrophilic and lipophilic balance of the supporting solid membrane (interaction with the support) [51][52] [49]. Solubilisation of LM into the feed side or the retentate side may be a problem too, if LM has not been chosen properly.

In operating conditions, if pore size distribution is narrow, one could use the Young-Laplace Equation to determine the limit transmembrane pressure at which one can work. Above this difference of pressure, LM would be mechanically removed from the pores.

$$\Delta p = \frac{4k_p \cos(\theta)\sigma}{d_p} \quad (1.2)$$

Where Δp is the difference of pressure, d_p is the pore diameter, θ is the contacting angle between the solid and the liquid, σ is the interfacial tension between LM and permeate/feed and k_p is a correcting factor between 0 and 1 [53]. From this equation can be stated that stability is increased by decreasing pore diameter and increasing surface tension.

The main techniques that are being applied to increase stability of SLMs are gelation of the LM [54], increase of tortuosity of the solid supporting membrane [55], coating the surface of the membrane with a thin protective film [56] and micro-encapsulated of LM [55]. The use of a high viscosity LM will also improve stability of the SLM [57].

Regarding to the application of SLMs to pervaporation, there is a major requirement that has to be fulfilled in order to ensure the stability of the SLM. Since vacuum is applied in the permeate side, part of the LM could be lost by volatilization. That's why low vapor pressure liquids are required [48]. The recently developed ionic liquids can fulfil this requirement.

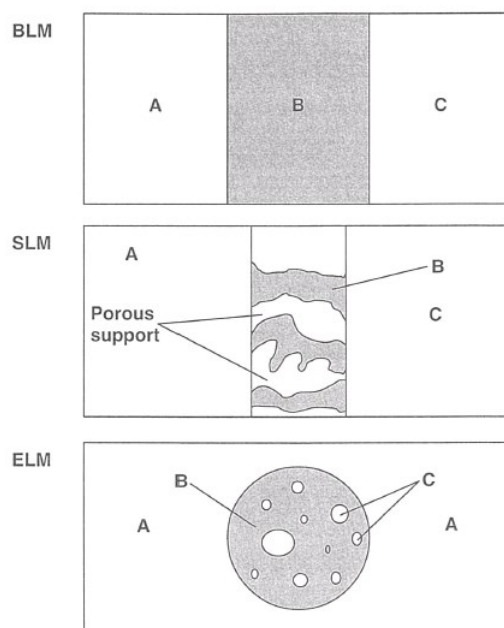


FIGURE 1.13: Scheme of a Bulk Liquid Membrane (BLM), Supported Liquid Membrane (SLM), and Emulsion Liquid Membrane (ELM) Systems. (a) is the feed, (b) is the liquid membrane and (c) is the permeate [46].

Ionic liquids

With solvents that widely have been used up to now, a broad range of different properties can be achieved. However, they all present in general a narrow interval of temperature in which they are liquid often between 75 and 200 °C. This limits their range of application since they are relatively volatile at working conditions. In order to avoid the negative economic and environmental impacts of these losses, a new type of solvents have received a lot of attention in the past decades. The so-called *Room Temperature Ionic Liquids* (IL). ILs are made of organic salts with a high degree of asymmetry. Due to this last feature, anions and cations can not pack to form crystalline structures at room temperature. As a consequence, ILs will stay as liquids with zero vapor pressure in a broad range of temperatures being stable up to temperatures higher of 400 °C [58]. On top of that, a huge number of possible combinations of cation and anion are available (almost a million of binary ILs) and ILs properties can be tailored by that choice [59]. See Figure 1.14 where are shown different cations and anions.

ILs can be designed (by choice of cation, anion and their substituents) in order to provide a selective solubility towards the target component. This which makes ILs very suitable solvents for separations of liquids and gases. Furthermore, some of them provide an enantioselective separation. ILs have also other intersecting properties such as capability of dissolving large amounts of polar and nonpolar compounds, high viscosity, high conductivity, good heat transfer properties, low flammability or low dielectric constant [60] [61]. These features increase the number of potential applications of ILs. Regarding to their drawbacks, ILs are still under research lacking data about their properties, corrosion and toxicity. They have a high cost as well [58].

To sum up, ILs seem to be a excellent type of liquids to be used in SLMs since they have low volatility, high viscosity and tailorable solubility which will ensure stability and selectivity of the SLM. Their high cost is not a problem since, in SLMs, only a small amount

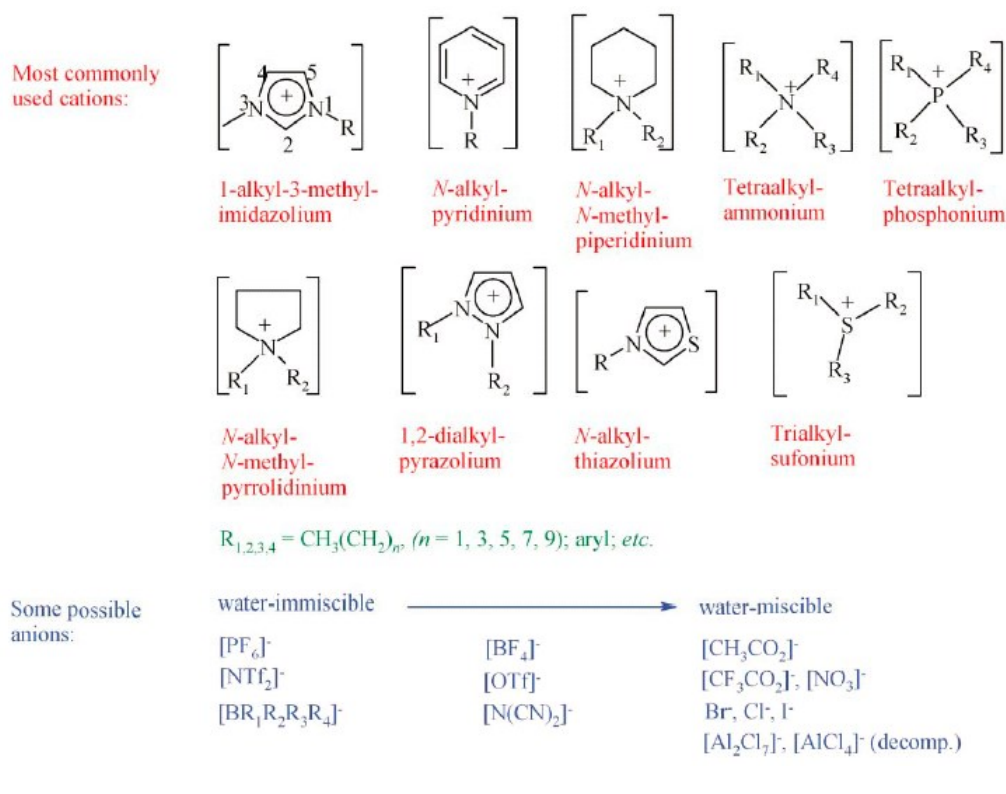


FIGURE 1.14: Examples of cations and anions used in ILs [59].

of IL is required.

1.5 Supported Ionic Liquid Membranes

Several studies have been performed in order to test the performance of *Supported Ionic Liquid Membranes* (SILM) in different applications [62]. Among these applications are separation of gaseous mixtures, receiving especial attention the recovery of CO_2 from gaseous streams rich on N_2 or/and CH_4 [63], recovery of ionic metals from aqueous solutions in which IL membranes characterise for being stable [64] and separation of organic components. Since this last application is very important for the case that is considered in this Master Thesis, it will be reviewed in more detail. Here, the attention is going to be focused in organophilic separations, i.e. extraction of organic components from a organic mixture. Since immobilisation of IL into the membrane is an important subject, it will be discussed as well.

1.5.1 Immobilisation of Ionic Liquids

One of the main questions that comes up when SILMs are considered is how to immobilise the ILs inside of the porous structure of the supporting membrane. Mainly three methods have been applied in literature to introduce the IL in the membrane. The first one is based on dipping the membrane into IL and waiting enough time to allow diffusion of IL inside of the porous structure [55]. The second method is based on applying pressure by N_2 on top of the membrane to force the IL to enter in the porous structure [65]. Finally, IL is placed over the membrane and vacuum is applied in order to remove the air from the pores and to suck in the IL [66].

IL viscosity is a very important factor in IL immobilisation and as consequence in SILMs stability. The higher the viscosity the more difficult is for IL to penetrate in the porous structure of the membrane. For high viscosity ILs it is recommend to use immobilisation under pressure since vacuum driven is rather difficult in this case. However, when low viscosity ILs are going to be used, vacuum techniques are more appropriated since they are easier to perform [65].

IL can be diluted in order to reduce immobilisation time by reducing viscosity as Kim et al [55] did. They studied CO₂/N₂ separation by IL immobilisation in a PVDF hollow fiber membrane. They diluted the IL in methanol (40 vol%) which has low surface tension with the material of the membrane and it is volatile. The IL was immobilised by putting in contact the membrane with this mixture either by injecting the mixture in the membrane (tube side) side or by dipping the membranes in the mixture (shell side). N₂ was used to remove the methanol afterwards. They found that impregnation by the shell side requires more time in order to be comparable to tube side impregnation due to diffusion of IL until the active layer.

Once IL has been immobilised, the excess of IL that is impregnating the membrane is removed to determine the amount of IL that has been immobilised. Cserjési et al. [67] investigated gas separation properties of SILMs for several types of ILs. In order to determine the amount of IL that is immobilised it was necessary to weight the membrane before and after impregnation removing the excess of IL carefully with a soft tissue. They observed that the thin blot membrane became transparent when pores were filled up of IL. Several authors followed the same procedure to determine the amount of IL that was immobilised. However it is expected that part of the supporter layer also contains IL and not just the active layer. Paul Scovazzo et al. [68] removed the excess of IL by letting wiping the membrane overnight. Hernández-Fernández et al. [65] computed this amount by using mass balances.

Hernández-Fernández et al. [65] compared pressure and vacuum driven immobilisation methods in SILMS. According to their results, higher stability and higher amount of ILs was achieved by using pressure driven immobilisation. They also performed SEM (Scanning Electron Microscopy) and EDXS (Energy Dispersive X-ray Spectroscopy) to characterise membrane surface before and after immobilisation. Pore filled up with IL were observed.

1.5.2 Application of SILMs in organic molecules separation

Since the use of SILMs does not require a large amount of energy or solvent it has received large attention as a suitable selective organic component separation technique. Five main cases have been investigated: transesterification reaction reactants and products, alcohols, organic acids, hydrocarbons and amines[69][62].

Branco et al. [70], selected a set of 7 representative organic chemicals (1,4-dioxane, propan-1-ol, butan-1-ol, cyclohexanol, cyclohexanone, morpholine and methylmorpholine) as organic mixture to be separated. They tested several combinations of ILs based in 1-(n-butyl or n-octyl or n-decyl)-3-methylimidazolium cations and PF₆ or BF₄ anions and supportive membranes materials (PVDF, PES, HPP, NHPP and nylon). SILMs were prepared by vacuum filtration and placed in a diffusion cell that separates the feed side and the permeate side, both sides containing diethyl ether. They shown that a right combination of IL and material support is very important to achieve a high selective separation towards the desired component. In another paper, Branco et al. [71] studied the separation of isomeric amines (hexylamine, diisopro-pylamine, and triethylamine) with [BMIm][PF₆] supported in a PVDF membrane. IL immobilisation method and experiments set-up were the same set-up than those described above. They found this SILM allows to separate secondary from primary and tertiary amines with a huge selectivity when separation of these components is

rather difficult for conventional separation techniques due to their close boiling point. They reported a good stability for this SILM.

Matsumoto et al. [72] investigated the separation of aromatic hydrocarbons by SILMs. In their study they used as LMs [BIMm][PF₆], [HMIIm][PF₆], [OMIm][PF₆] and [Et₂MeMeON][TNf₂] supported in a PVDF porous membrane. The immobilisation method was not explained. These SILMs were placed between two liquid phases, the feed phase made of heptane in which aromatic hydrocarbons (benzene, toluene and p-xylene) were dissolved and the receiving phase that was hexadecane. Overall mass transfer coefficients were computed and compared to the case where water was used as LM. Lower fluxes and higher selectivities towards heptane were achieved by using ILs instead of water. This is attributed to a lower viscosity of water. For SILMs, it was observed that the larger is the hydrophobicity of the IL used, the higher is the permeation rate. Finally, [HMIIm][PF₆] provided the best selectivity, speciality for benzene. Matsumoto et al. [73] also reported selective separation of organic nitrogen components from n-heptane mixtures by using SILMs based on 1-alkyl-3-methylimidazolium cation and quaternary ammonium anions. Those ILs which a stronger hydrophilic character led to higher selectivity.

Zhang et al. [74] tested how selective the separation of toluene-cyclohexane mixtures by SILMs is. They used [BPy][BF₄] and [BMIm][BF₄] as ILs. Both were immobilised in a PVDF hollow fiber membrane by impregnation during 30 min. In this case, the toluene-cyclohexene mixture was in the tube side and n-dodecane, the receiving phase, flowed through the shell side. They studied the effect of variables such as temperature, initial concentration of toluene and flow rates in both sides in the flux and the selectivity. They found that selectivity of separation of toluene ranged between 5 and 11.5, increasing when the toluene concentration in the feed is decreased. However, flux is lower when concentration is lower. Regarding to the temperature, they show that the higher it is, the better is the mass transfer. Finally, their SILMs presented stability at long term operations (100 h).

De los Ríos, Hernández-Fernández and coworkers [75] [76] [77] [78] [79] [80] have published several articles in selective separation of transesterification reactants and products by using SILMs. Relevant information from their research is summarised in Table 1.4. In all their experiments SILMs were prepared by applying nitrogen pressure (2 bars). This process was repeated three times in order to ensure a good penetration of the IL in the pores. The excess of IL was removed by dripping over night. In order to study the selective permeation of species, a diffusion cell was used in which both feed and receiving phase were n-hexane. In 2007 [75] (see Table 1.4), they tested several types of membrane materials (hydrophobic and hydrophilic) and they found important differences in permeability in the case of hydrophilic membranes, especially when nylon was used. That's why in posterior studies they always used this material. These SILMs showed a good stability as well. In 2008 [77], they investigated the influence of the IL hydrophobic / hydrophilic character in the permeability of the different components. They found that the higher the hydrophilic character of the IL is, the better the separation due to an increase in permselectivity is. In 2009 [78] they tested 14 ILs showing that selectivity is mainly influenced by the choice of anion and that better selectivities are achieved by using cations with shorter alkyl chain length. Dialkylimidazolium based cations allowed more selective separations than alkylpyridinium based cations. Finally, in 2010 [80], they studied more in depth the separation of 16 different components important in transesterification reactions (reactants and products). They looked to the variation of permeability with the alkyl chain length of a given type of organic component. According to their results, there is not only difference of permeability for different types of organic components (different functional groups) but also, inside of a given type, the shorter is the alkyl chain length the larger is the permeability.

In 2007, by using the same experimental set-up (diffusion cell using n-hexane as feed and receiving phase) and immobilisation methods (nitrogen pressure driven and dripping

TABLE 1.4: Summary of De los Ríos, Hernández-Fernández and coworkers's work in selective separation of transesterification reactants and products by using SILMs.

Components	IL	Membrane material	Source
Vinyl butyrate, 1-butanol, butyl butyrate and butyric acid	[BMIm][PF6]	PVDF, PTFE, PC, nylon	[75] [77] [78] [79]
	[OMIm][PF6]	nylon	[75] [77] [78] [79]
	[BMIm][PF4]	nylon	[77] [78] [79]
	[OMIm][PF4]	nylon	[77] [78] [79]
	[BMIm][NTf2]	nylon	[77] [79]
	[OMIm][NTf2]	nylon	[77] [79]
	[BMIm][Cl]	nylon	[78]
	[EMIm][EtSO4]	nylon	[78]
	[BMIm][MeSO4]	nylon	[78]
	[BMIm][EtSO4]	nylon	[78]
	[BMIm][OcSO4]	nylon	[78]
	[BMIm][MDEGSO4]	nylon	[78]
	[EMPy][EtSO4]	nylon	[78]
	[BMPy][BF4]	nylon	[78]
	[BMIm][DCA]	nylon	[78][79]
	[BMIm][NO3]	nylon	[78]
	[OMIm][DCA]	nylon	[79]
16 different organic chemicals (vinyl and aliphatic esters, alcohols and carboxylic acids)	[BMIm][PF6]	nylon	[76]
	[OMIm][PF6]	nylon	[76]
	[BMIm][PF4]	nylon	[80]
	[OMIm][PF4]	nylon	[80]
(R,S)-1-phenylethanol, (R,S)-1-phenylethyl propionate, Vinyl propionate and Propionic acid	[BMIm][PF6]	nylon	[81]
	[OMIm][PF6]	nylon	[81]
	[BMIm][PF4]	nylon	[81]
	[OMIm][PF4]	nylon	[81]
	[BMIm][NTf2]	nylon	[81]
	[OMIm][NTf2]	nylon	[81]

overnight) as described above, Hernández-Fernández et al. [81] combined kinetic resolution of a racemic 1-phenylethanol mixture (carried out by transesterification with vinyl propionate and lipases as biocatalyst) with SILMs in a membrane bioreactor in order to provide a selective separation. Information about SILMs tested is also available in Table 1.4. They reported that there is not a selective separation between enantiomers for any of the SILMs that were tested. However, differences in permeability between each type of component (ester < acid < alcohol) was found. SILMs based on [BMIm][BF4] had the highest average permselectivity. The average permselectivity was dependent on hydrophilicity of the immobilised IL. Following the same research subject, in 2009 Hernández-Fernández et al. [82] studied the separation of the same system using [BMIm][BF4] supported in a nylon membrane. Water content and alkyl chain length of the vinylic ester influence in kinetic resolution was studied. They found that the coupling of enantioselective lipase catalysed reaction combined with SILMs provided an interesting method for enantioselective production of organic compounds.

There is not a large number of publications about organophilic separations with SILMs. For this reason, it is the aim of this work to contribute to this unexplored field. To do so, in this master thesis the performance of SILMs in the separation of reactants and products

of the transesterification reaction used to produce glycerol carbonate from dimethyl carbonate and glycerol is going to be tested. The SILMs will be prepared by combination of two membrane supports, one hydrophilic and another hydrophobic, and six different ILs. Effect of temperature, feed composition and choice of anion and cation in the performance will be discussed and the effectiveness of the preparation procedure will also be addressed.

Chapter 2

Experimental work

2.1 Materials and chemicals

Two types of supporting solid membrane were tested: a polyacrylonitrile (PAN) flat ultrafiltration membrane (hydrophilic) purchased from SYNDER FILTRATION (USA) and a polypropylene (PP) flat microfiltration membrane (hydrophobic) model ACCUREL® PP 1E (R/P) provided by 3M GmbH (Germany). Regarding to the LMs, 6 ILs were studied: 1-Octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([OMIm][NTf2]), 1-Dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C12MIm][NTf2]), 1-Octyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [OMPyrr][NTf2], Trihexyltetradecylphosphonium chloride ([P66614][Cl]), 1-Octyl-methylimidazolium bromide ([OMIm][Br]) and 1-Octyl-methylimidazolium triflate ([OMIm][OTf]). All ILs were synthesised by Certech (Belgium) and have a purity larger than 95 %. Methanol (99.8 %) was provided by VWR INTERNATIONAL and Dimethyl Carbonate (99 %) from Alfa Aesar.

The Cations and anions of the ILs that have been used in this study are shown in Figure 2.1 with the exception of the [C12MIm] cation whose structure is analogous to [OMIm] (or [C8MIm]).

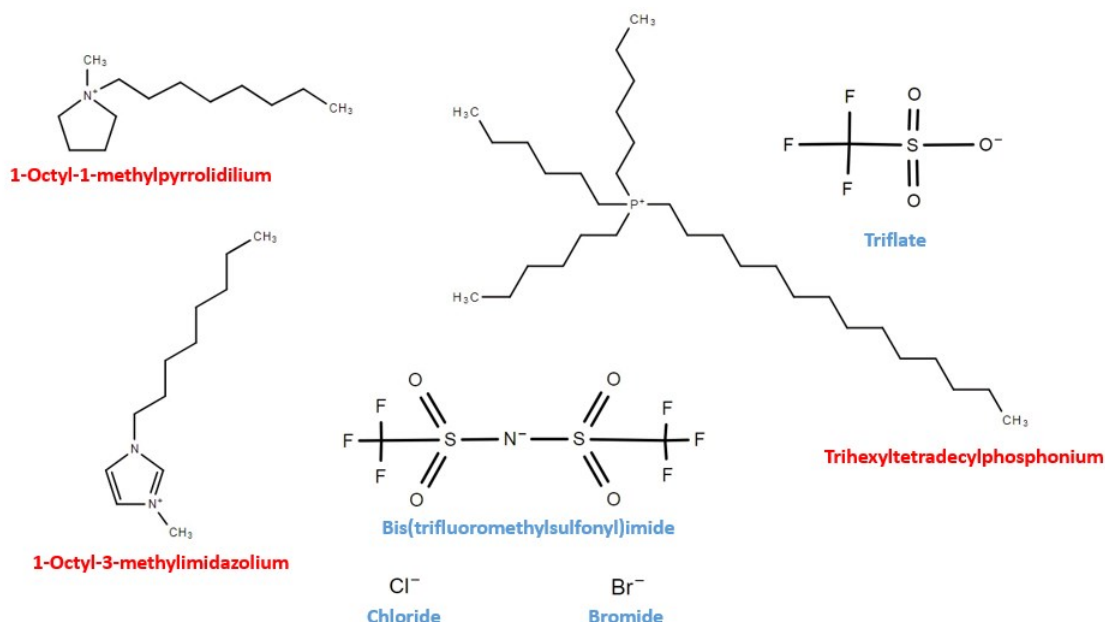


FIGURE 2.1: Cations and anions of the ILs under study. Cations in red and anions in blue.

An important point in every study related to ILs is the justification of the selection of those ILs. In this case, the selection process of the ILs is not part of this work since they had been selected before. However, for a better understanding a brief discussion is provided in what follows. The 6 ILs of this study were selected because, for some of them, it was found in the literature that they have some affinity with MEOH. In principle this is indicating that MEOH will permeate through SILMs made with these ILs. For the rest, as in many publications related to ILs, they haven't been manufactured to test what happens since there is not so much information about them in the literature. On top of that, before this work began, the SILMs under study have been already tested with a quaternary mixture of GL, DMC, GC and MEOH. Only DMC and MEOH were obtained in the permeate being GL and GC rejected by these SILMs. For that reason, this study is going to be focused on the separation performance of binary mixtures of DMC and MEOH which makes the analysis more simple. Therefore, results from this work provide information about the capability of these SILMs in breaking the azeotropic point of DMC - MEOH mixture.

2.2 Experimental set-up

A scheme of the experimental set-up that was constructed by SUIZER CHEMTECH AG (Switzerland) is shown in Figure 2.2. It consists of a steel membrane cell where the membrane is placed on top of a metallic porous disc which provides support to the membrane, a feed tank where the solution to be separated is stored, a condenser used to condense the vapor permeate which is a glass bottle submerged in a cryogenic bath (unistat cc huber from Huber), a vacuum pump (2 stages vacuum pump model VE2350 purchased from Thermo Fisher Scientific) to create vacuum in the permeate side of the membrane and a pump (regenerative turbine pump model HT-NPY-2251 from SPECK Pumpen) that transports the retentate back to the storage tank. Several valves and sensors of temperature (Digital thermometer GMH 3230 from GREISINGER Electronic, Germany), pressure (absolute pressure sensor model DVR2 provided by VACUUBRAND GMBH & CO KG ©) and volumetric flow (mechanical indicator DK34 from KROHNE Messtechnik GmbH) allow to control the system. The temperature of both, the feed tank and the condenser, can be fixed and controlled automatically. Finally, the feed tank temperature is controlled by a heating bath containing oil (heating bath with coil, internal pump and stirrer Julabo, model MA from Huber). This set-up is used for SILMs preparation, stability and separation performance tests.

2.3 Membrane preparation

PP and PAN membranes were tested as supporting material with every IL to produce SILMs. To do so, the following procedure was applied: in the first place a circular flat membrane whose dimension fitted in the membrane cell was prepared by cutting from the commercial membrane roll. Then the membrane was weighted with an analytical balance (DeltaRange® AE 260 METTLER purchased from METTLER TOLEDO) and placed in the membrane cell on top of the porous metallic disc. Vacuum was applied in the permeate side to facilitate the membrane placing by turning on the vacuum pump and opening valve 1 and 3 while valve 2 was closed (see Figure 2.2). An elastic ring seal was placed in the peripheral part of the membrane in the membrane cell to ensure a good seal. The following was to put the desired IL on top of the active layer of the membrane using a plastic pipette. The amount has to be enough to cover completely and homogeneously the surface of the membrane. Next, the membrane cell was hermetically closed. Valve 2 was regulated to fix 50 mbar of pressure in the permeate side. As a consequence, the immobilisation process began and lasted 2 h. Once that immobilisation finished, vacuum was broken by opening valve 2 completely and

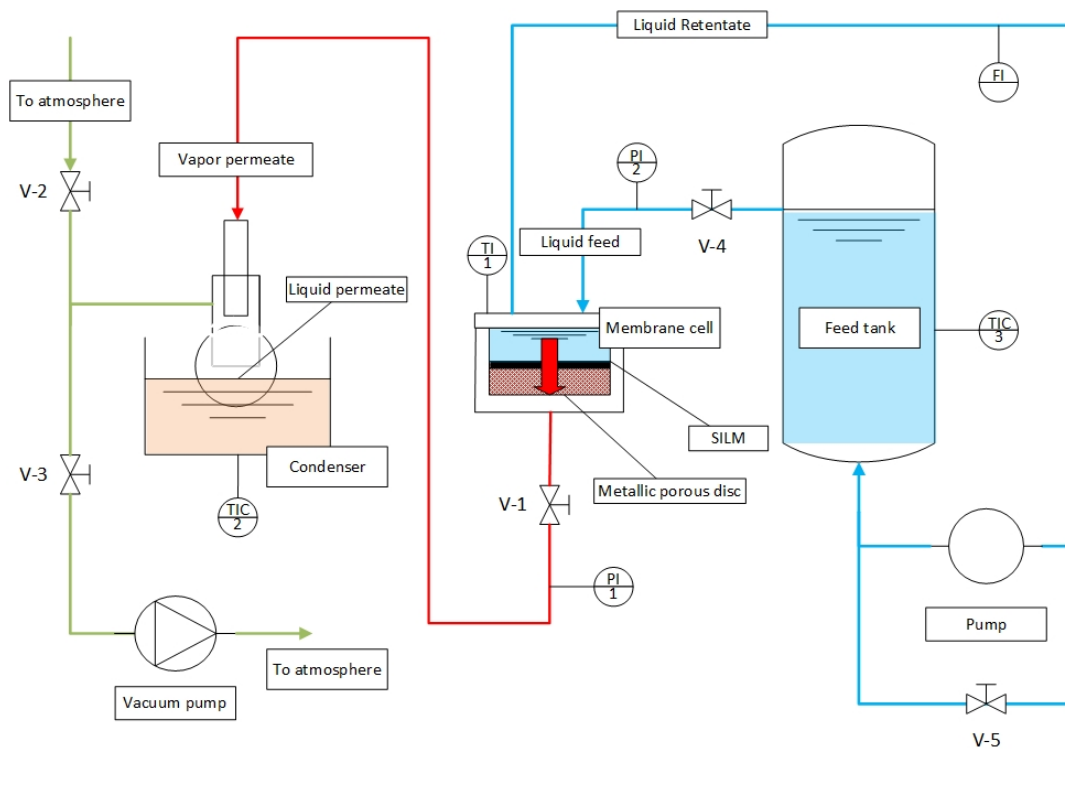


FIGURE 2.2: Scheme of the experimental set-up.

the membrane was removed from the membrane cell. The excess of IL over the membrane was removed carefully using paper. Finally, the membrane was weighted again and stored in paper. Since ILs are not volatile, special conditions of storage were not required.

Since ILs are not volatile it was very important to avoid contamination to clean the membrane cell and porous metallic disc with ethanol and change globes after every experiment.

In order to qualify the performance of the immobilisation procedure, before testing SILMs stability, SILMs cross section was observed and compared to the cross section of a PAN membrane without IL by using Scanning Electron Microscopy (SEM). This tool allowed to look at the pores of the active layer in order to check if they were filled up with ILs. Firstly, SILMs were cut with a knife and placed in a sample holder vertically. Before being introduced in the SEM device they were covered with conducting coating. However, with this method the cross section of membranes were deformed by the process of cutting. For that reason, another procedure of sample preparation was followed. In this method, SILMs were immersed into nitrogen liquid. Since the polymeric material from which they are made up is very brittle at such low temperatures, samples were broken without deforming the cross section.

2.4 Stability tests with pure MEOH and DMC

SILMs stability under pure solute conditions (MEOH/DMC) and SILM-MEOH and SILM-DMC interaction without coupling effects were tested by measuring the steady state flux of pure solute at different temperatures (30, 40 and 50 °C) for the ILs [OMIm][NTf2] and [OMIm][Br]. To do so, a SILM that was previously prepared is placed in the experimental set-up. Here, complete vacuum was applied (valve 2 completely closed) and valves 4 and 5 were opened while the pump was working. This allowed the pure MEOH/ pure DMC to

circulate in the system. No liquid permeate was recovered (placing the permeate bottle out of condenser) until the desired temperature in the cell (Temperature sensor 1) was reached. To reach faster this temperature the pump worked at 80 % of its maximal speed, which increased turbulence in the system, and the temperature of the heating bath was fixed high enough to overcome the heat losses. Once that the desired temperature has been reached, the permeate bottle was placed in the condenser which was usually between -20 and -30 °C and flow was regulated and kept between 80 and 90 L/h by valve 5 and adjusting the speed of the pump. This value was high enough to reduce the mass transfer resistance in the feed side and, in the case of a multicomponent feed, it eliminated the gradients of concentration in region near to the surface of the membrane. These gradients create a back diffusion flow that reduces the net flux through the SILM. This phenomena is known as concentration polarization. Every 30 min or 1 hour (depending of the amount of permeate), the bottle was replaced by a new one and the weight of the condensed permeate was measured. This procedure continued up to 3-4 h which was the time that normally takes to reach steady state when there was a constant flux and operating parameters were stable. The average of the last values of flux is the steady state flux.

2.5 Separation performance tests with a binary MEOH-DMC mixture

To conclude, separation tests with the binary mixtures were performed in order to study the effect of feed concentration in separation performance (coupling effects) and the effect of cation and anion choice in selectivity. To do so several binary mixtures of DMC and MEOH were prepared (20, 50 and 80 % of DMC in mole fraction) and tested with different ILs ([OMIm][NTf2], [OMIm][Br], [OMIm][OTf] and [OMPyrr][NTf2]). Experiments were carried out at 30 °C for every IL. Regarding the experimental procedure, it was almost the same as the previous pure MEOH and DMC experiments described above. In this case the permeate was weighted and some samples (one from the feed and two from the permeate) were also taken and frozen in order to be analysed afterwards by Gas Chromatography to measure the concentration of MEOH and DMC in order to compute the partial flux of each compound.

Chapter 3

Theory

3.1 The solution-diffusion model

Figure 3.1 represents a SILM separating the feed and permeate phases. Black lines are an approximate representation of the gradients of concentration across the system as a consequence of the transport resistance through the SILM. This transport comprises several steps. First, the solute (DMC or MEOH) is transported from the bulk liquid phase by convection until it reaches the active layer of the membrane. Then, sorption takes places in a stepwise fashion. First, a molecule of solute breaks its connections within the feed phase. Second, the solvent (IL) makes room for the solute. Finally, the solute establishes new interactions with the solvent. The two first steps are endothermic while the third one is exothermic. Then, the solute travels along the pores full of IL by diffusion until it reaches the back side of the membrane. Afterwords, the solute evaporates. The last step is the transport by convection until the bulk vapor permeate phase. In order to evaluate this transport the solution-diffusion model is going to be used. This model was developed for the study of transport through dense membranes but it has been successfully applied to SILM pervaporation experiments as well [69].

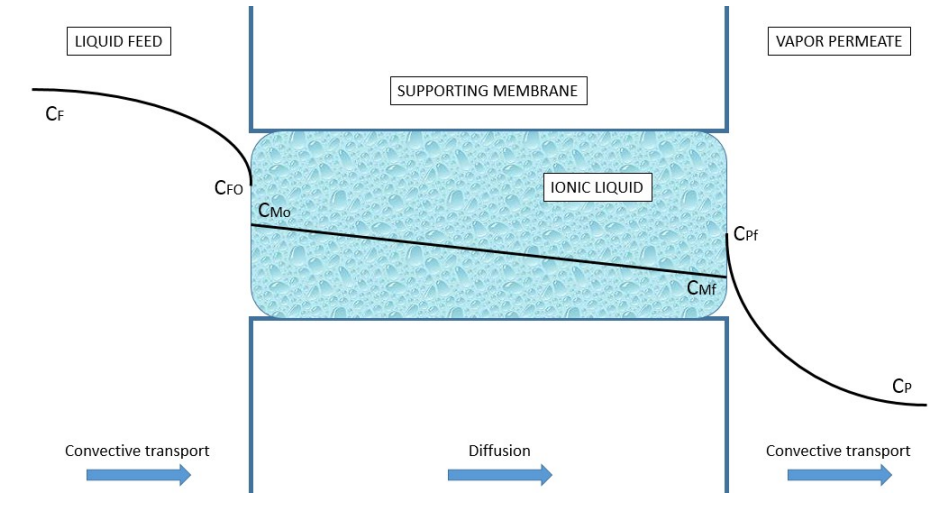


FIGURE 3.1: Scheme of a SILM used in pervaporation.

In contrast to the expression of this model applied to pervaporation of a multicomponent mixture that has been already discussed in the Literature Study, this chapter provides a more developed expression by include all parameters that are going to be measured and computed.

$$J_i = \frac{P_{LM_i}}{l_{LM}} (\gamma_i x_i P_i^s - y_i P_T) \quad (3.1)$$

Where J_i is the flux of the specie i , P_{LM_i} is the permeability of i through the LM, l_M is the thickness of the LM, γ_i is the activity coefficient of the specie i in the liquid feed, x_i is the molar fraction of the specie i in the liquid feed, P_i^s is the saturation pressure of the specie i at the temperature of the liquid feed, y_i is the molar fraction of the specie i in the vapor permeate and P_T is the total pressure in the permeate side. In this model, mass transfer resistance in the feed and permeate side have been neglected ($C_F=C_{F0}$ and $C_P=C_{Pf}$). This can be achieved by fixing appropriate experimental conditions. These are a high turbulence in top of the membrane by using a high speed and a powerful vacuum pump that removes immediately the permeate vapor from the membrane surface. It is also assume that feed and permeate vapor partial pressures are in equilibrium with the concentration within the IL in the feed and permeate side respectively. As a consequence, mass transfer resistance comes from the diffusion inside of the IL.

The main disadvantage with the use of permeability is that it is required to know the thickness of the LM which it is expected to be different for every IL and it could be not homogeneous in the whole membrane. For these reasons, the equation can be simplified by the use of permeance of component i , $\bar{P}_{LM_i}$, in which this length is included.

$$J_i = \bar{P}_{LM_i}(\gamma_i x_i P_i^s - y_i P_T) \quad (3.2)$$

Since permeability is the product of sorption and diffusion coefficients, $P_{LM_i} = S_i D_i$, the inverse of permeance is proportional to the mass transfer resistance. As a consequence, it is expected that flux is improved by a high solution capacity (high partition coefficient) and low viscosity of the IL [83]. It is important to estimate this parameter since permeance gives the performance of the SILM without taking into account the driving force (difference of vapor partial pressure in the feed and permeate side). Since the total pressure in the permeate side is very low in comparison with the saturation pressure the expression can be further simplified. The remaining terms of the equation can be expressed in terms of activation energies if one wants to study the effect of temperature.

$$J_i = J_{0i} \exp\left(\frac{-E_{Fi}}{RT}\right) \quad (3.3)$$

$$\bar{P}_{LM_i} = \bar{P}_{0i} \exp\left(-\frac{E_{S_i} + E_{D_i}}{RT}\right) = \bar{P}_{0i} \exp\left(\frac{-E_{Pi}}{RT}\right) \quad (3.4)$$

$$P_i^s = A_i \exp\left(\frac{-\Delta H_{vap_i}}{RT}\right) \quad (3.5)$$

Where J_{0i} , $\bar{P}_{0i}$ and A_{0i} are constants, E_{Fi} , E_{S_i} , E_{D_i} are the activation energy of flux, sorption (heat of solution or dissolution) and diffusion respectively and ΔH_{vap_i} is the enthalpy of vaporisation. The sum of the activation energies of sorption and diffusion is the activation energy of permeation, E_{Pi} . As the enthalpy of vaporisation is a positive value, the driving force always increases with temperature. E_{M_i} is the heat of mixing and is computed as the difference between the heat of dissolution and enthalpy of vaporisation. E_{M_i} contains information about the interaction of the solute (MEOH or DMC) and the solvent (IL) [83] [84]. Separating the effects of sorption and diffusion by calculating both activation energies requires to perform experiments that are beyond the scope of this thesis. Instead, activation energy of diffusion is going to be computed by using two empirical correlations that allow to estimate the diffusion coefficients of MEOH and DMC in ILs. The first one is the Scheibel equation [85] whose expression is the following:

$$D_{iIL} = C \frac{T \left(1 + \left(3 \frac{V_{mIL}}{V_{m_i}} \right)^{2/3} \right)}{\eta_{mIL} V_{m_i}^{1/3}} \quad (3.6)$$

Where D_{iIL} is the diffusivity of i in the IL under study in cm^2/s , η_{IL} is the viscosity of the IL in $mPas$, T is the temperature in K , V_{IL} and V_i are the molar volumes of IL and solute i in cm^3/mol . C is equal to 2.7×10^{-7} for ILs [86]. The second one was provided by Morgan et al. [86] for imidazolium based ILs. The expression provided by them is not an explicit function of temperature since it is applied to 303.15 K. However, as it was proposed in [87], one may assume a linear dependence of diffusivity and temperature giving the following equation:

$$D_{iIL} = 5.28 \times 10^{-18} \frac{T}{\eta_{IL}^{0.66} V_{m_i}^{1.04}} \quad (3.7)$$

Where D_{iIL} is in m^2/s , η_{IL} is in Pas , T is in K , V_{IL} and V_i is in m^3/mol . Empirical correlations to compute the density and viscosity values required by these expressions are available in the Appendix A.

3.2 Separation efficiency

The ideal/real selectivity and the separation factor defined as follow are important among the parameters that can quantify the performance of the separation.

$$\alpha_{ij} = \frac{\bar{P}_{LM_i}}{\bar{P}_{LM_j}} \quad (3.8)$$

$$\beta_{i/j} = \frac{y_i/y_j}{x_i/x_j} \quad (3.9)$$

The ideal selectivity does not take into account coupling effects (interaction between i and j in the transport through the SILM) as permeances are computed using the flux of the pure components. However, the real selectivity uses the partial flux of components i and j to compute the permeances since the feed it is a multicomponent mixture. The partial flux of a given specie is computed using the total flux and its weight fraction in the vapor permeate.

Chapter 4

Results and discussion

4.1 Membrane preparation results

To guarantee to success of the immobilisation process a constant value of pressure (fixed around 50 *mbars*) is displayed in Pressure sensor 1 during 2 h. If this happens, there is a strong interaction between the supporting membrane and the IL. When there is a low interaction or a repulsion between support and LM, due to different hydrophobic/hydrophilic character, the IL passes through the supporting membrane and the porous metallic disc as IL is being sucked by the vacuum. The membrane is not capable to hold the IL. In consequence, pressure in the permeate side continuously increases due to a reduction of the pressure drop across the membrane. For the ILs that were selected for this study, any of them was held by the PP membrane (hydrophobic) which demonstrates that they have a hydrophilic character. For the case of the PAN membrane, immobilisation worked for every IL except for [C12MIm][NTf2]. For this IL the formation of a thick layer of crystals in the surface of both membranes was observed. The observation of the crystallisation process is coherent with the fact that the melting temperature of the IL is 292.4 K (19.25 °C) [88]. While the experiment was performed, ambient temperate was below that value. The presence of impurities in the IL could also contribute to this phenomenon as it is well known that impurities have a large influence in IL properties [89]. Once that the immobilisation finished, the amount of IL immobilised was computed by difference of weight of the membrane before and after the test, these results are shown in Table 4.1 .

TABLE 4.1: Results of membrane preparation.

Ion liquid name	Initial weight [g]	Final weight [g]	Amount of IL [g]	Viscosity at 298 K [<i>mPas</i>]
[OMIm][NTf2]	0.4397	0.6933	0.2536	95 [90]
[OMPyrr][NTf2]	0.4376	0.7120	0.2744	112 [91]
[C12mim][NTf2]	0.3987	0.6010	0.2023	155 [92]
[OMIm][OTf]	0.4025	0.5876	0.1851	492 (293 K) [93]
[P66614][Cl]	0.4352	0.6019	0.1667	1683 [94]
[OMIm][Br]	0.4146	0.5728	0.1572	5068 [95]

As expected based on the literature, in general, the larger the viscosity of the IL the lower the amount of IL that is immobilised in the membrane for the same membrane preparation conditions (2 h and 50 *mbar*). The larger the viscosity the more difficult it is for the IL to penetrate in the pores of the porous membrane because of the capillary force [65].

For [OMIm][Br] which is the most viscous, another two set of membrane preparation conditions were tested: 2 h at 15 *mbar* and 4 h at 50 *mbar*. Results are summarised in the Table 4.2. From these results one could argue that immobilisation time is more important than the level of vacuum that is applied since for the case of 4 h there is the largest amount of IL inside of the membrane. However, during the experiments in which SILMs stability was tested with pure DMC, see next section, both SILMs (4 h and 50 *mbar* and 2 h and 15

mbar) provided values of flux (under the same conditions of driving force and flow) that lead to a the contrary conclusion since the flux was higher for the SILM prepared during 4 h at 50 *mbar*. The larger the amount of IL immobilised in the membrane, the larger the distance is that components that are dissolved into the IL have to travel by diffusion and, as a consequence, the lower the flux. It is important to point out that the measurement of the amount of IL immobilised inside the membrane are not very accurate since even after cleaning the surface with a soft tissue the immobilisation there is always some IL that is left in the surface. This phenomenon has been observed multiple times, specially when one SILM is prepared and stored in paper in order to be used in the next day. Comparing the weight just after cleaning with a soft tissue and the weight just before the SILM is going to be tested there is always a significant reduction of weight. So, as the level of vacuum seems to be more important, SILMs containing the more viscous [OMIm][Br] IL were prepared always during 2 h at 15 *mbar* to ensure a good immobilisation.

TABLE 4.2: Results of membrane preparation with different immobilisation parameters.

Preparation conditions	Initial weigh [g]	Final weight [g]	Amount of IL [g]
2h and 50 mbar	0.4156	0.5728	0.1572
2h and 15 mbar	0.4106	0.5349	0.1243
4 h and 50 mbar	0.4526	0.6235	0.1709

In order to provide a solid prove that ILs are actually in the pores of the supporting membrane, cross-sections of SILMs were observed using SEM. Both methods, direct cutting with a knife and immersion in liquid nitrogen before cutting, led to cross-section deformation specially for direct cutting. The best images are available in the Appendix C, mainly from the method that used liquid nitrogen. It is possible to see the IL inside of the porous structure just by comparing the SILM cross-section pictures with the pictures of the fresh PAN membrane without IL (C.1a and C.1b). The active layer is difficult to see in some pictures but in case of fresh SILMs part of the support layer is also filled up with IL. This is not observed in the PAN membrane without IL. From these images one can conclude that the immobilisation procedure works.

It is also possible to see in Figure C.2a the presence of a thick layer of IL in the SILM top surface and in the cross-section. This SILM was observed using SEM some hours after it was prepared. As it was discussed above, this thick layer can lead to errors comparing the amount of IL that has been immobilised.

4.2 Pure solute tests

During all the experiments performed with the two SILMs containing [Omim][Br] and [Omim][NTf2] for both solutes (MEOH/DMC) and at three different temperatures there wasn't any presence of liquid permeate after several hours of testing. This means that only vapor permeate is passing through the SILM. For this reason, these SILMs are stable since ILs are not washed out from the pores of the support membrane by the feed phase or mechanically removed by the difference in pressure. Used SILMs cross-sections were observed using SEM (see Appendix C). IL was not observed filling in the pores. Although comparing their weight with the fresh PAN membrane, IL was still present. A large amount of IL is washed in the first experiment although they are yet stable.

Regarding the measurements performed during these experiments, as an example, Figure 4.1 shows the time evolution of the flux of pure MEOH through a SILMs containing [OMIm][NTf2] at the studied temperatures. The rest the Figures are in the Appendix B.

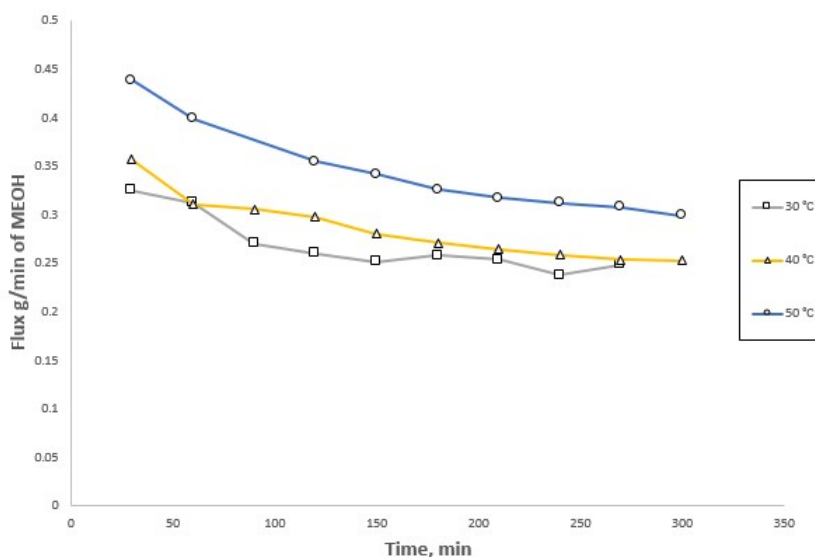


FIGURE 4.1: Evolution of MEOH flux through a SILM containing [OMIm][NTf2], prepared during 2 h at 50 mbar, at 30, 40 and 50 °C.

One can see in these Figures that most of the curves follow a similar trend in which flux decreases with time until it reaches a stationary value. This is due to the evolution of the driving force across the SILM. At the beginning, the IL inside of the pores is pure. This improves the extraction of feed components at the beginning. However, once the SILM is in contact with the feed, the feed components (in this case there is only one solute) will start to dissolve and to diffuse through the pores filled up with IL. As a consequence, concentration of MEOH/DMC in the IL will increase. An analogous process happens in the permeate side. At the beginning the partial vapor pressure of these components in the permeate side is zero which favours the stripping process. With time the gradients of concentration are reduced until steady state is reached.

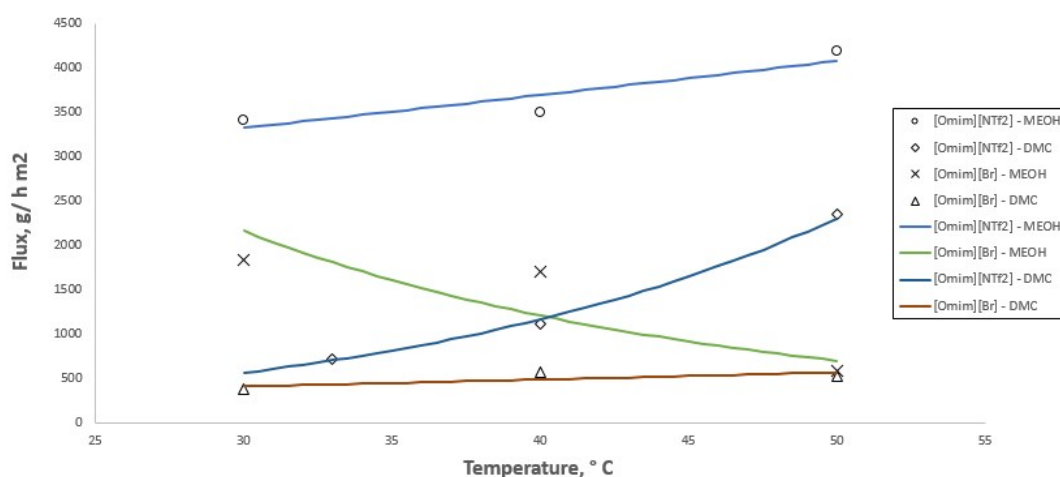


FIGURE 4.2: Evolution of the steady state flux of pure MEOH and DMC through a SILMs made of PAN containing [OMIm][NTf2] or [OMIm][Br] with temperature.

The relationship of the steady state flux with temperature for both SILMs can be seen in Figure 4.2. Markers represent the experimental points while the solid lines are computed using the Arrhenius type equation of flux provided in the Theory section (Equation 3.3). The parameters of this equation are computed by linear regression to the experimental data ($\ln(J)$ vs $1/T$). Several conclusions can be extracted from these results. First of all, as the general trend that appears in the literature, the larger the temperature, the larger the flux. This is associated to an increase of the driving force, (saturation pressure of feed side), a decrease of the viscosity of IL and an increase of the free volume in the SILM due to thermal mobility when temperature increases [83] [96] [97]. Second, a surprising result is observed with the SILM containing [OMIm][Br] tested with MEOH. In this case the steady state flux value decreases as temperature increases. This behaviour has not been reported in the literature and is very interesting since it is the contrary effect when this SILM is tested with DMC. In consequence, increasing/decreasing temperature will promote the separation of one component and hinder the separation of the other. The experiment was repeated in order to confirm this trend.

As explained in the Theory section the flux contains also the effect of the driving force. So, one should use permeance in order to quantify the transport through the SILM independently of the driving force. Figure 4.3 contains this information. Markers represent the experimental points while the solid lines are computed using the Arrhenius type equation of permeance provided in the Theory section (Equation 3.4). The parameters of this equation are computed by linear regression to the experimental data ($\ln(P)$ vs $1/T$).

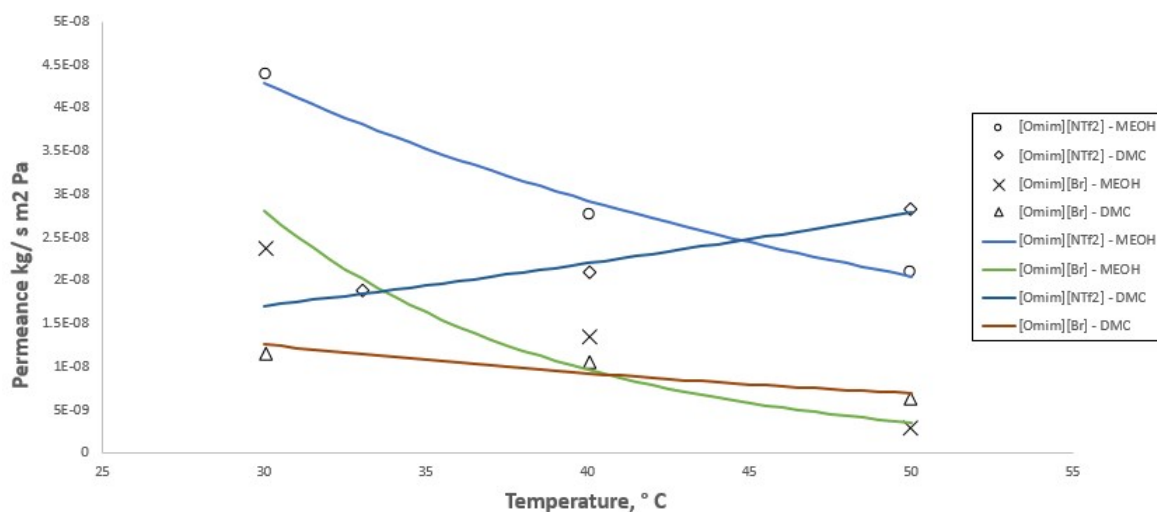


FIGURE 4.3: Evolution of permeance of pure MEOH and DMC through SILMs containing [OMIm][NTf2] or [OMIm][Br] with temperature.

Permeance decreases with temperature for every SILM excepts for the SILM with [OMIm][NTf2] tested with DMC. For the first cases, sorption contribution is larger than the diffusion contribution to the permeability [83]. For this reason, even when diffusion is improved by increasing the temperature the detriment of the exothermic sorption is more important. However, this is not the case for the SILM with [OMIm][NTf2] tested with DMC. In this case two things can happen, either the diffusion is more important than the exothermic absorption or the absorption is endothermic and is promoted by increasing the temperature. The fact that diffusion is dominating over sorption can be due to a low interaction between the solute and the IL [98]. One may estimate the activation energy of diffusion, hence the activation

energy of sorption, by computing the diffusion coefficient at different temperatures using the correlations provided in the Theory section (Equations 3.6 and 3.7).

TABLE 4.3: Diffusion coefficients for MEOH in [OMIm][NTf2] and [OMIm][Br] computed using the Scheibel equation (Formula 1) and Morgan correlation (Formula 2). Diffusion coefficients are in m^2/s .

Temperature	[OMIm][NTf2]		[OMIm][Br]	
	Formula 1	Formula 2	Formula 1	Formula 2
30 °C	3.20663E-10	3.08629E-10	3.29223E-11	7.43332E-12
40 °C	4.3604E-10	4.89208E-10	5.60939E-11	1.65783E-11
50 °C	5.8179E-10	7.53963E-10	9.24787E-11	3.51975E-11

TABLE 4.4: Diffusion coefficient for DMC in [OMIm][NTf2] and [OMIm][Br] computed using the Scheibel equation (Formula 1) and Morgan correlation (Formula 2). Diffusion coefficients are in m^2/s .

Temperature	[OMIm][NTf2]		[OMIm][Br]	
	Formula 1	Formula 2	Formula 1	Formula 2
30 °C	1.49623E-10	1.5775E-10	1.53617E-11	3.87219E-12
40 °C	2.03351E-10	2.49985E-10	2.61599E-11	8.63463E-12
50 °C	2.71176E-10	3.85175E-10	4.31048E-11	1.83292E-11

Some values of diffusion coefficients are presented in Table 4.3 and 4.4. Regarding the results, these values are consistent with the order of magnitude of diffusion coefficient of organic liquids in ILs. This order of magnitude is about $10^{-11} m^2/s$ [87]. Comparing the results of both equations, they provide close values for [OMIm][NTf2] but no so close for [OMIm][Br], specially for the diffusion coefficients of DMC in this IL. As expected, since MEOH molecules are smaller than the DMC ones, diffusion coefficients of MEOH in both ILs are higher. In addition, diffusion coefficients of MEOH and DMC are higher in [OMIm][NTf2] than in [OMIm][Br] which is logical because the later is much more viscous [86]. Before comparing the conclusions obtained from these values and the experimental results one has to realise that the empirical correlations were developed for diluted solutions. In the case of a larger concentration of solute, diffusion coefficients can be much larger due to the reduction of viscosity, steric effects and possible attractive or repulsive forces between components [99]. Here it is going to be assumed that these equations are valid. As consequence, the last conclusion related to the viscosity of ILs is in line with the permeance values obtained experimentally since MEOH and DMC permeance is higher in SILMs with [OMIm][NTf2] than with [OMIm][Br] (see 4.3). However, when permeance of MEOH and DMC in the same IL are compared, experimental results are not completely consistent. For example, for [OMIm][NTf2] MEOH permeance is higher than DMC permeance below 45 °C which is in line with the values of Tables 4.3 and 4.4 since MEOH molecules are smaller than DMC molecules. But above this temperature, permeance of DMC is higher. As it has already been explained, permeance also includes the sorption contribution which could be the reason of this behaviour and the decrease of permeance with temperature. Activation energy of flux, permeation, diffusion (using the average of both empirical correlations) and sorption (difference between the permeation activation energy and diffusion activation energy) are shown in Table 4.5 in order to provide a better understanding of the transport inside the SILMs.

In Table 4.5 positive values of activation energy indicate that the process is activated by increasing the temperature. From the activation energy of diffusion, it is clear that diffusion is more difficult in [OMIm][Br] than in [OMIm][NTf2] and that diffusion of MEOH is

TABLE 4.5: Activation energy of flux, permeance, diffusion, sorption or dissolution and heat of mixing.

J/mol	[OMIm][NTf2]		[OMIm][Br]	
	MEOH	DMC	MEOH	DMC
E_F	8289.83	57227.90	-45785.24	13051.92
E_P	-30006.14	19903.75	-84196.98	-24416.71
E_D	30805.96	31047.24	47275.93	47683.91
E_S	-60812.10	-11143.49	-131472.91	-72100.62
E_M	-24137.38	24668.01	-94798.194	-36289.12

easier than diffusion of DMC in both ILs for the reasons that have already been explained. Sorption is deactivated by temperature for every case. For DMC in [OMIm][NTf2] diffusion contribution is higher than sorption contribution to the permeance while for the rest, sorption is dominating permeation. The different values of activation energy shown in Table 4.5 have an appropriate order of magnitude compared to other values have been reported in literature [83] [96] [97]. For the case of MEOH in [OMIm][NTf2], it is possible to check how correct the assumptions are that have been taken to estimate the activation energy of sorption. Deng et al. [100] measured the heat of mixing of several combinations of alcohols and 1-alkyl-methylimidazolium bis(trifluoromethylsulfonyl)imide based ILs. Among these mixtures they also studied the MEOH - [OMIm][NTf2] mixture from which they reported the heat of mixture for several binary mixture compositions. Since the composition inside of the LM is unknown, one may take the highest value of heat of mixing. This value is 2453.71 [J/mol] (endothermic) for a composition of 55 % in IL (equation fitting experimental data is available in Appendix). This value is quite far from the heat of mixing value shown in 4.5 (exothermic) for this mixture. This means that the activation energy of diffusion that was computed assuming low concentration of solute in the IL is not correct. In fact, this activation energy is much lower which is indicating a faster diffusion. For MEOH in [OMIm][Br] sorption activation energy, or enthalpy of solution, is so high (exothermic) that it overcomes the driving force and diffusion causing a decrease of flux with temperature. The reason behind this behaviour is difficult to explain for several factors. First of all, to the best of my knowledge, it has not been documented in literature any similar case. Secondly, [OMIm][Br] is an IL that has not been extensively studied in the literature. Next, due to timing and limitations with the amount of IL it was not possible to perform other experiments such as sorption tests to explain this behaviour. However, using the information that is available in the literature it is possible to find some possible explanations. In previous computations it has been assumed that diffusion is activated by increasing temperature, so it is expected that the sorption step is exothermic and hindered by an increase of temperature. In other words, dissolving MEOH in [OMIm][Br] releases heat as both components have a strong interaction as shown by the negative value of heat of mixing. The enthalpy of sorption or solution has to be larger than the sum of the diffusion energy activation and the heat of vaporisation in order to justify the experimental results. In order to evaluate this enthalpy of sorption and how it is affecting the transport one should consider the interaction between [OMIm][Br] and MEOH molecules. Due to the lack of information in the literature about [OMIm][Br], the analyses was focused on [OMIm][Cl]. As it is discussed in the literature, it seems that the anion is playing the major role in IL properties and the alkyl length of the cation (octyl in this case) has a secondary role [58]. However, Br and Cl anions are similar enough to use this approximation. To explain MEOH - [OMIm][Cl] interaction, activity coefficients, excess molar volumes and excess molar enthalpies of the binary mixture [OMIm][Cl] - MEOH will be addressed. This information is contained in Figures 4.4 and 4.5).

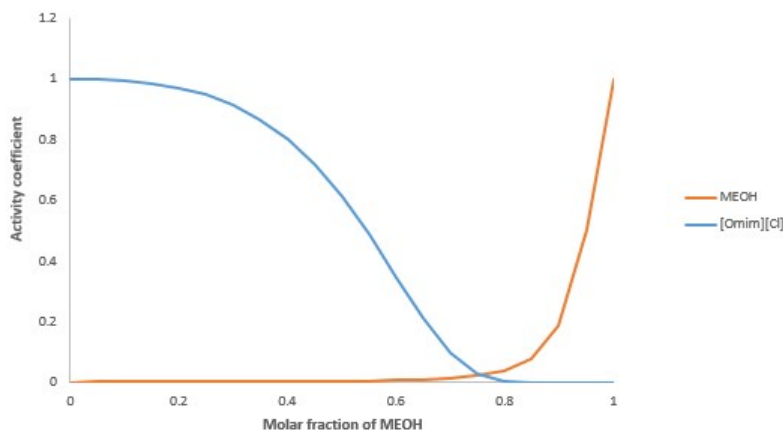


FIGURE 4.4: Activity coefficients of MEOH and [OMIm][Cl] in a binary mixture of both components at 298.15 K.

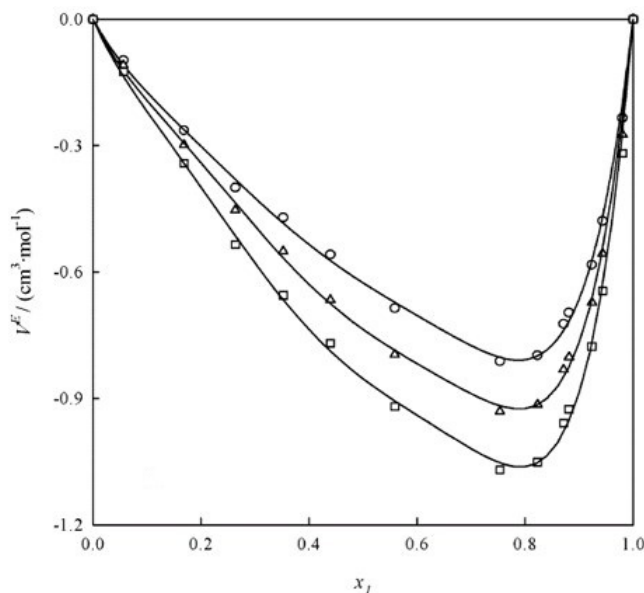


FIGURE 4.5: Molar excess volumes of binary mixtures of MEOH and [OMIm][Cl] at different temperatures, 298.15 K ●, 313.15 K ▲ and 328.15 K ■ [101]. x_1 is the molar fraction of methanol.

From Figure 4.4, in which activity coefficients were computed using the NRLT model (see Appendix), it is easy to see that the activity coefficients are always lower than the one indicating a negative deviation from the Raoult's law due to a strong interaction between MEOH and [OMIm][Cl] [102]. On top of that, the activity coefficient of MEOH sharply decreases as [OMIm][Cl] content increases which is indicating a very strong deviation from the ideal behaviour. This result is also confirmed by the negative excess molar volume values shown in Figure 4.5. Negatives values of excess molar volume are related to strong solute - solvent interactions and large differences in molar volume of solute and solvent molecules providing more efficient packing [101] [103]. However, in the later case a asymmetric "S" shape graph is observed [100] which is not the case here. Also, the excess mixing energies of

binary mixtures of dialkylimidazolium chloride ILs with alcohols are negative which indicates a strong interaction between them [104]. This strong interaction is the reason of these anomalous behaviour in temperature dependence of flux.

The comparison of interactions of ILs with MEOH and DMC without coupling effects can be discussed by looking to the mixing enthalpies in Table 4.5. From these values it is extracted that MEOH interaction with both ILs is stronger than for DMC since its heat of mixture is more negative. This can be due to several factors. The first one, MEOH is more polar than DMC which in principle should provide an stronger electrostatic ion-dipole interaction with ILs than in the case of DMC. MEOH dipole moment is 1.7 D while for DMC it is 0.9 D [105]. Second, MEOH molecules are smaller and can pack better between the molecules of IL. This is possible because ILs are nanostructured liquids [106]. A last factor is the capability to form hydrogen bonds with the ionic species. So MEOH would have stronger hydrogen bonds with the ILs than DMC. This effect will be explained in more detail later. By comparing the interaction of MEOH and DMC with both ILs it is clear that they have a stronger interaction with [OMIm][Br]. Anion size is very important with respect to water solubility of ILs. That's why [Br] based ILs are soluble in water while [NTf2] based ILs are insoluble [89]. As a consequence, [OMIm][Br] is more hydrophilic than [OMIm][NTf2]. This can be observed by looking to their water-octanol partition coefficients, K_{WO} (more information about the interpretation of these coefficients in Appendix A and Table A.4). For [OMIm][Br] $\log K_{WO}$ is equal to -4.5 while for [OMIm][NTf2] is between 0.8 and 1.04. Regarding to MEOH ($\log K_{WO} = -0.81$) and DMC ($\log K_{WO} = 0.354$), they have high solubility in water as they are hydrophilic. For this reason it was expected that they have a larger affinity with [OMIm][Br] as the values of heat of mixing prove. To ensure that these results are consistent one can check other solubility parameters such as Hildebrand, Hansen and Kamlet-Taft solvation parameters for the four components (see Tables A.3 and A.5 in Appendix A for more information about these parameters). Hansen and Hildebrand parameters seem to indicate that DMC has a stronger affinity with [OMIm][NTf2] and MEOH with [OMIm][Br] which is in agreement with water-octanol partition coefficients. However, there are some discrepancies in the values of these parameters coming from different authors. Hildebrand and Hansen solubility parameters are useful to guess if two compounds are soluble and, as other solubility and polarity scales, some contradictory predictions can happen [107].

From Kamlet-Taft solvation parameters one could guess what the main interactions are between the IL and the solute molecules (see Table A.5 in Appendix A). [OMIm][Br] (O = octyl) is assimilated to [HMIm][Br] (H = hexyl) in this case. [HMIm][Br] has a high value of dipolarity as all ILs due to its nature as ionic species and it has larger hydrogen bond basicity than acidity. Hydrogen bond basicity is linked to the [Br] anion and hydrogen bond acidity is related to the C-H in the imidazolium ring [108]. However [OMIm][NTf2] has larger hydrogen bond acidity than basicity. In this case hydrogen bond basicity comes from the oxygen atoms in the anion [109]. Regarding to the solute, DMC has zero hydrogen bond acidity and MEOH has a strong hydrogen bond acidity character. MEOH has a larger value of dipolarity compared to DMC as it has been already discussed using dipole moment values. From this we can conclude that MEOH has a stronger interaction with the ILs compared to DMC due to its higher dipolarity and its capability to form hydrogen bonds. DMC could form also hydrogen bonds but only by acting as hydrogen bond acceptor while MEOH can perform both roles. MEOH has larger affinity towards [OMIm][Br] because they can make easier hydrogen bonds since one has hydrogen bond acidity (hydrogen bond donor) character while the other has hydrogen bond basicity (hydrogen bond acceptor) character. Finally, according to these parameters, DMC will interact preferentially with [OMIm][NTf2] due to its hydrogen bond basic character. These results are coherent with the information provide by several authors.

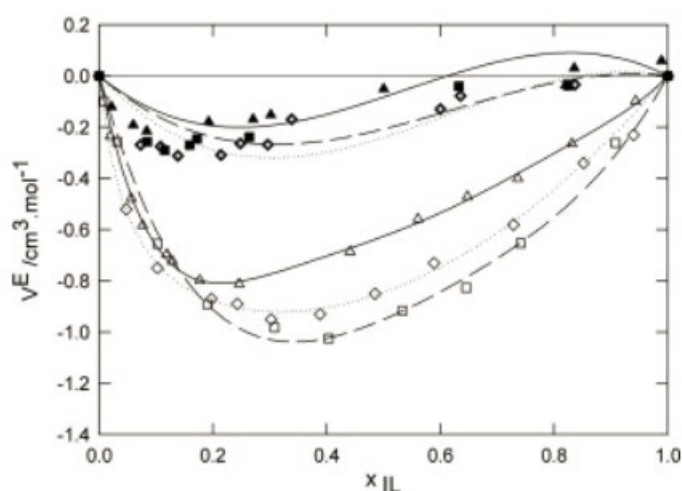


FIGURE 4.6: Molar excess volumes of binary mixtures of MEOH - [OMIm][Cl], $\triangle$ and MEOH - [OMIm][NTf2], $\blacktriangle$ [110].

Hanke et al. [110] performed molecular simulation of binary mixtures of dialkylimidazolium chloride and different solutes in order to determine the solution mechanism. They found that for hydrogen bonding solutes such as water and methanol, there is a stronger interaction with the chloride anion due to hydrogen bonding. But for polar non hydrogen bonding solutes such as dimethyl ether (which in this case could be assimilated to DMC), the interaction is stronger with the imidazolium ring and it is mainly due to dispersion and electrostatic forces. This interaction is between the oxygen atom of dimethyl ether molecule and the hydrogens of the imidazolium cation. Hydrogen bonding solutes were more soluble in the ILs. Alcalde et al. [111] studied [BMIm][NTf2] - ethanol mixtures by molecular dynamics. They found that the energy of interaction of cation and anion was very large compared to the interactions of both ions with the solute. Regarding to solute interaction with cation and anion, ethanol forms hydrogen bonds with both but those formed with the anion are stronger. All these interactions are stronger than the hydrogen bonds between ethanol molecules. As a consequence, one can expect that the interaction of MEOH and [OMIm][Br] is larger than the interaction with [OMIm][NTf2]. This is in agreement with the information shown Figure 4.6, the excess molar volume of the binary mixture [OMIm][NTf2] - MEOH is lower than for a binary mixture of [OMIm][Cl]. This coincides with the conclusions that can be formed from the mixing enthalpies estimated in this work in Table 4.5. Why DMC seems to have a stronger interaction with [OMIm][Br] than [OMIm][NTf2] according to Table 4.5, when solubility scales point in the contrary direction, can be due to the assumptions that were taken during the computation of activation energy of diffusion.

Regarding to the separation performance, the ideal selectivity can be estimated using the values of permeance of pure components, meaning that there are no coupling effects between MEOH and DMC. The evolution of the ideal selectivity with temperature is shown in Figure 4.7. This is computed as the permeance of pure MEOH divided by the permeance of pure DMC. For both SILMs, the ideal selectivity decreases increasing temperature. Here it presents the usual trade-off between selectivity and flux for the SILM containing [OMIm][NTf2]. In the case under study (GC recovery), it is more interesting to separate the byproduct MEOH from the reaction medium than the reactant DMC as this drives the reaction to the right and allows to reduce the needed excess of DMC. Since the increase of flux of MEOH for the SILM containing [OMIm][NTf2] with temperature is not very important it is

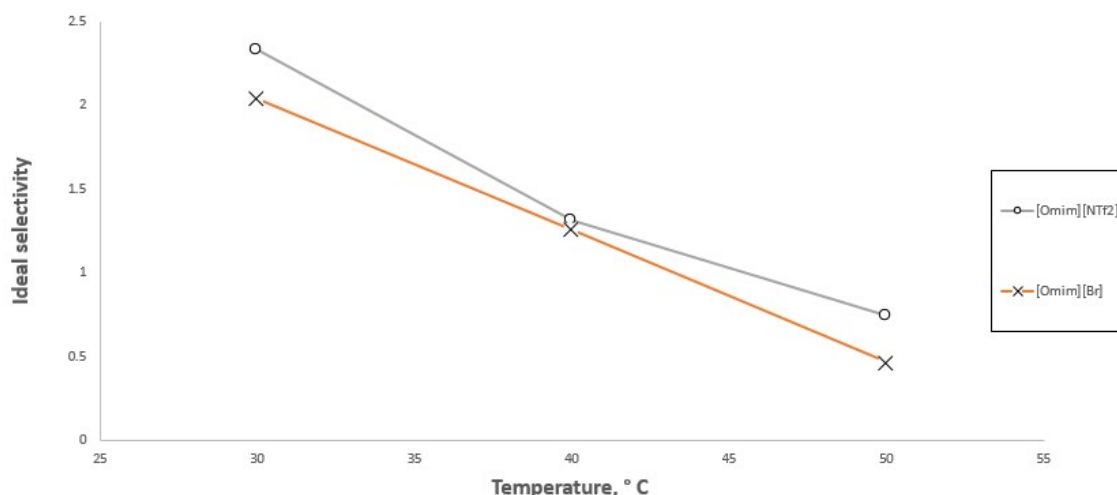


FIGURE 4.7: Evolution of ideal selectivity with temperature.

more interesting to work at lower temperature to keep a good selectivity. For the case of the SILM containing [OMIm][Br] which has a unusual trend (decreases of flux when increasing temperature in the case of pure MEOH), this trade-off is not present. As a consequence, if one wants to remove preferentially MEOH from the reaction medium and at high flux it is better to work at low temperature and at high temperature only when it is interesting to recover the DMC.

4.3 Binary mixture tests

SILMs that contained [OMIm][NTf₂], [OMIm][Br], [OMIm][OTf] and [OMPyrr][NTf₂] were tested at three different feed compositions at 30 °C in order to see the effect of feed composition and cation/anion choice in separation performance. In the Appendix B the evolution of total flux with time for every experiment is presented. In order to compute the permeance of every component it is necessary to calculate the partial fluxes of each component. These values are obtained from the steady state flux and the molar fractions of MEOH and DMC in the permeate measured by Gas Chromatography. The molar fractions of MEOH and DMC in the feed and permeate of every experiment are in the Table B.1 in the Appendix B. In what follows only permeance, selectivity and separation factor are going to be discussed. Figure 4.8 shows the permeance of DMC and MEOH at different feed compositions for SILMs containing [OMIm][NTf₂] and [OMPyrr][NTf₂]. Permeance is expressed in GPU units as most of authors do which allows to compare these results with the literature. "1GPU = 3.35x10⁻¹⁰ mol/(m²sPa)" [112]. For [OMIm][OTf] any flux wasn't obtained after several hours at different compositions. In the case of [OMIm][Br] after one experiment in which flux was so small that it was not possible to measure its composition it was decided to stop studying this IL. Low availability of time and very small amount of IL to prepare more membranes justified this decision.

Figure 4.8 shows that both ILs, with the exception of [OMPyrr][NTf₂] tested with a feed composition of 20 % of MEOH, followed a similar trend in which the permeability is favoured for DMC with respect to MEOH. Also, the larger the concentration of MEOH in the feed the better the permeability of both components. The anomalous value of permeance for [OMPyrr][NTf₂] tested with a feed composition of 20 % of MEOH is probably due to the immobilisation process. The ring seal used to place the membrane in top of the porous

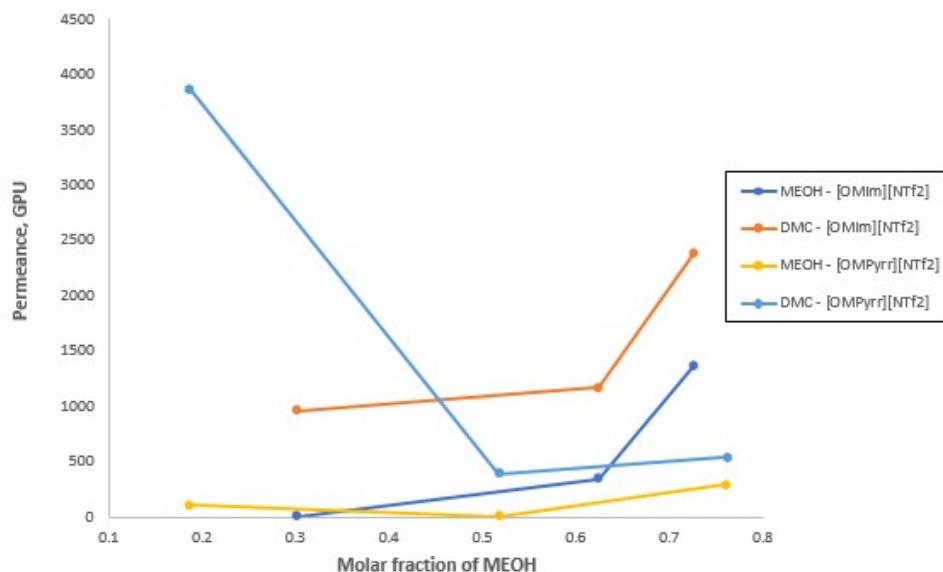


FIGURE 4.8: Permeance of MEOH and DMC for [OMIm][NTf2] and [OMPyrr][NTf2] at different feed compositions.

metallic disc was broken and replaced by a new one. This one fitted better in the membrane cell avoiding that some IL could wet the supported layer of the membrane. For this reason this value is not truly comparable to the rest since the set-up was different. Regarding to the effectiveness of the separation, Figures 4.9 and 4.10 show how selectivity and separation factor vary with feed composition.

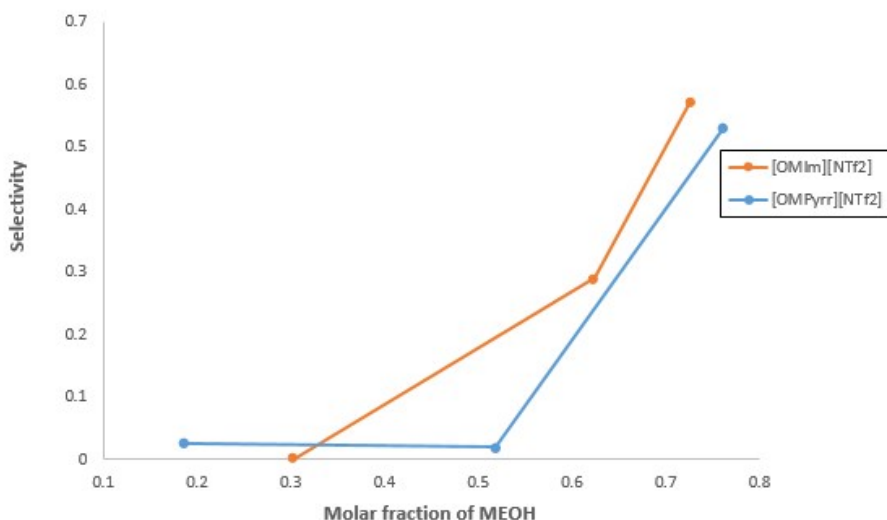


FIGURE 4.9: Selectivity of MEOH for [OMIm][NTf2] and [OMPyrr][NTf2] at different feed compositions.

As can be seen in the Figures, both parameters have the same evolution. The larger they are the better the separation is for MEOH. In order to know the selectivity and separation factor for DMC, it is the inverse of what is shown in the Figures. The main conclusion of this figures is that the selectivity of MEOH is low in the whole range of composition. But

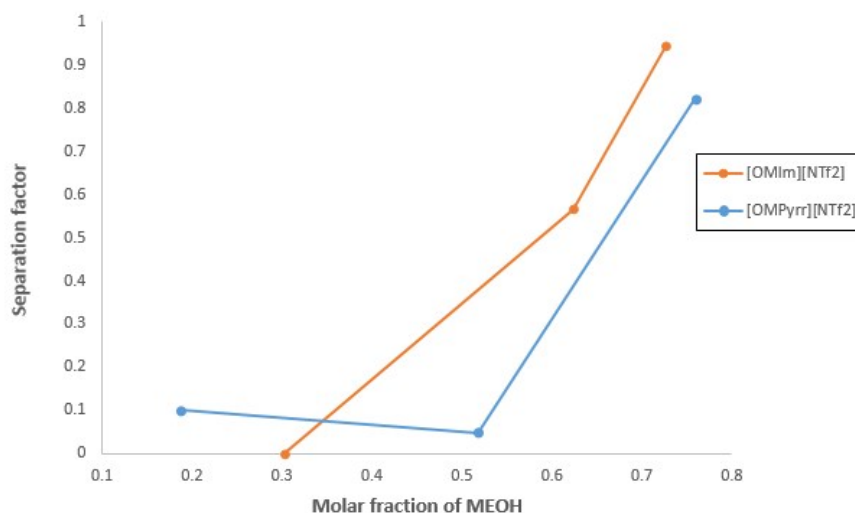


FIGURE 4.10: Separation factor of MEOH for [OMIm][NTf2] and [OMPyrr][NTf2] at different feed compositions.

for DMC, a really high value of selectivity and separation factor is obtained for low MEOH concentrations. Since the azeotropic point of the MEOH - DMC mixture is at 86.47 % of MEOH (in molar basis) these SILMs are not appropriated to its separation. However, since they do not permeate GC they could be useful in the purification of this compound from the reaction mixture. Both ILs show a similar behaviour which is coherent with literature since the anion plays the mayor role in solubility and these ILs only differ in their cation. It is evident that DMC have a strong interaction with these ILs. First because of its larger value of permeance compared to MEOH and second because increasing DMC concentration reduces dramatically the MEOH permeance. Looking to the values of $\log P_{O/W}$, Kamlet-Taft solvation parameters and δ_{Hil} , that were discussed in the previous section, they are consistent. So there is a strong coupling effect since pure MEOH permeance is higher than pure DMC permeance but this is inverted in the binary mixture. This can be explained analysing to the interactions of the MEOH - DMC - IL. From the experimental data one can deduce that MEOH has a stronger interaction with DMC as the larger is DMC concentration the lower is MEOH permeance. On top of that, at 80 % mol of DMC, MEOH do not permeate at all and stay in solution while DMC permeates with the same values of flux as if it was pure. At low concentration of DMC, MEOH molecules still interact with the ionic liquid and they permeate dragging more DMC molecules with them which explains the higher permeance of both components at low DMC concentrations. The slightly lower values of permeance of DMC and MEOH for [OMPyrr][NTf2] compared to [OMIm][NTf2] are justified by its higher hydrophobic character [113].

For [OMIm][OTf] SILMs there is no flux which means that MEOH and DMC have a stronger interaction between them than with this IL. This is not supported by the literature. Domanska et al. [114] computed the activity coefficients at infinite dilution of different solutes in [BMIm][OTf]. They found negative values of activity coefficients for methanol which indicates a strong interaction. This interaction was related to the hydrogen bonds formed between the hydrogen group of methanol and the anion. Li et al. [115] studied the vapor - liquid equilibrium of the ternary system: MEOH - DMC - [HMIm][OTf]. They proved that the activity coefficients of MEOH and DMC in the binary mixture decrease with the increment in [HMIm][OTf] concentration. Also, they found a stronger interaction of this IL with DMC than with MEOH. In addition, in a scale of hydrophilicity, [OMIm][OTf]

is between [OMIm][NTf2] (immiscible with water) and [OMIm][Br] (miscible with water) [116].

Regarding to the SILM containing [OMIm][Br], according to the results a very small flux was obtained. In consequence, one could also conclude that DMC and MEOH have a stronger interaction between them than with the IL. However, this is contradicting the values of heat of mixing shown in Table 4.5. Zhang et al. [117] investigated the separation of MEOH - DMC mixtures with [EMIm][Br] and [BMIm][Cl]. Although these two ILs are not truly representative of [OMIm][Br] because of the large difference in cation alkyl chain, however one can use them as comparison. These authors found that both ILs have a stronger interaction with MEOH which is consistent with Table 4.5. Since only one experiment was performed it is difficult to conclude that this result is reliable.

Finally, one should realise the complexity of interactions that takes place in the separation including MEOH - DMC - IL - supporting membrane interactions. This makes it more difficult to elucidate what is actually happening inside of the SILM. In order to know it, more experiments are required. In any case, the fact that anion has the mayor role in solubility is clearly shown in these experiments.

4.4 SILM change in performance

This section is dedicated to explain some unexpected changes in SILM separation performance found during pure solute and binary mixture experiments.

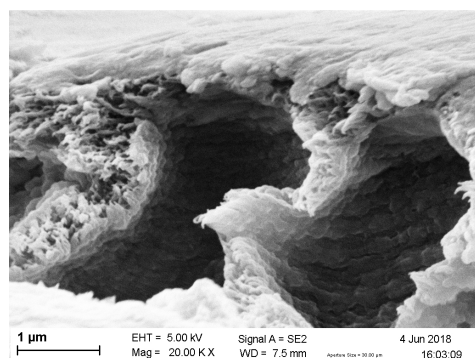
An unexpected effect was observed when the tests of SILM containing [OMIm][NTf2] were performed with MEOH at 60 °C. No flux was obtained which is not consistent with the trend of increasing flux with temperature that appears at 30, 40 and 50 °C. On top of that, it was observed multiple times that once that one SILM reached that temperature it could not be used anymore since no permeate was obtained at lower temperatures. No flux was also observed in a [OMIm][Br] containing SILM with MEOH at 60 °C. But, this value of flux is consistent with the trend of this IL. Several factors could be the reason behind this unexpected effect that has not been reported in the literature. First, the temperature is near the MEOH boiling point. If vapor is formed in the feed phase it could avoid or hinder the contact of the feed solution with the SILM. However, once that the membrane is tested at 30 °C one should again obtain permeate which is not the case. Second, MEOH is immiscible with [OMIm][NTf2] at that temperature. Crosthwaite and coworkers have studied the liquid phase behaviour IL - alcohols mixtures [118] [119]. These mixtures usually have a upper critical solution temperature (UCST) at lower IL concentration. In other words, above this temperature both components are completely miscible, but below, phase separation takes places. In top of that, this temperature is below 30 °C for small chain alcohols and long alkyl chain ILs. As a consequence, MEOH and [OMIm][NTf2] should be miscible in the whole range of experimental temperatures. The irreversible character of this effect could imply that a chemical reaction is happening. In fact, a change of membrane surface color was observed when it was tested at high temperature with MEOH (see Figure 4.11). The PAN membrane was white before the test.

[OMIm][NTf2] starts to decompose at 618 K [91] so decomposition of the IL is not a possible explanation. Gelation of the IL decrease the flux [54]. IL gelation can take place in different ways: addition of low molecular weight chemicals [120], incorporation of inorganic particles [121], mixing with polymers [122], polymerisation of the IL [123] and mixing different ILs [124]. Although the behaviour of [XmIm][NTf2] - alcohols mixtures have been studied [100] [119], it has not been reported that MEOH acts as a gelatin agent of these ILs. Furthermore, no nanoparticles were added to the membrane and this IL does not contain vinyl groups to promote self polymerisation. In addition, since it has been already explained,

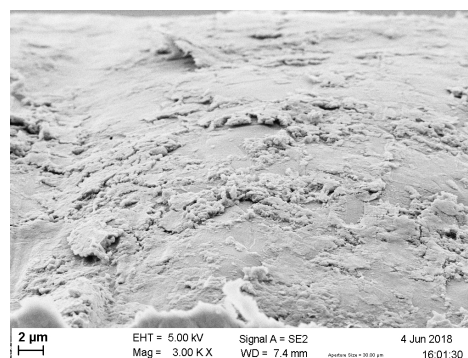


FIGURE 4.11: SILM, [OMIm][NTf₂] immobilised in a PAN membrane, after 60 °C with MEOH.

much care was taken in order to avoid contamination of other ILs. Finally, no polymer was added to the IL and the membrane is made of a cross-linked material. Otherwise, the membrane would have been dissolved by the MEOH or DMC. For these reasons, gelation of the IL is not the cause. PAN membrane deterioration by reaction with MEOH or modification due to high temperature seems unlikely. PAN has a high chemical resistance due to the strong interaction between its -CN groups. In the case of water, it is necessary to reach temperatures up to 120 °C to form CN-OH interactions [125]. However, the presence of IL could catalyse some reaction that modified the supporting material and as a consequence changes the separation performance of the SILM. The cross-section of a SILM that was tested at 60 °C was observed using SEM to find the cause of this behaviour.



(A) Cross-section.



(B) Membrane surface.

FIGURE 4.12: Used SILM with [OMIm][NTf₂] after test with MEOH at 60 °C prepared by immersion in liquid N₂ and cutting with knife.

In Figure 4.12 no IL was observed in the pores. Also, several cracks were observed in the surface of the membrane that were not observed for the fresh SILM or fresh PAN membrane without IL. This could be indicating a different behaviour of the membrane during the process of cutting. This would be related to the change of composition of the supporting material.

Another phenomenon that was also unexpected was related to the sudden change of separation performance of some membranes. For example, some membranes were stored after their use and some weeks later they didn't provide permeate anymore. Although no

experiment was performed in order to discover the cause, one possible explanation is the absorption of atmospheric water of the SILM. It has been indicated in the literature that ILs are quite hygroscopic, even the hydrophobic ones. In fact, IL can increase its water concentration in a 5 % in weight after 3 hours of exposure [89]. In top of that, IL properties depends a lot in their impurities such as water. As a consequence, an increase of water content would change SILM separation performance and stability [62]. Chemical analysis tools such as SEM-EDS could provide a better understanding of this phenomenon.

Chapter 5

Conclusions

Separation performance of binary mixtures of MEOH and DMC by different SILMs has been addressed. First IL immobilisation was studied as first screening step for the different SILMs. Second, SILM interaction with DMC and MEOH without coupling effects was investigated through pervaporation experiments with pure DMC and MEOH. They were performed at different temperatures to analyse the temperature effect as well. Finally, separation performance was studied through pervaporation experiments with the binary mixtures in order to evaluate the presence of coupling effects and their feasibility in separation of MEOH and DMC mixtures.

In the first place, IL immobilisation in two different supporting materials: PP and PAN was studied. Any IL was held by the PP membrane indicating their hydrophilic character. It was observed that the larger the viscosity the lower the amount of IL that was immobilised. SEM images of SILM cross section allowed to see pores filled with IL. Secondly, pervaporation experiments with pure methanol and dimethyl carbonate were carried out at three different temperatures (30, 40 and 50 °C) with two SILMs containing [OMIm][Br] and [OMIm][NTf2]. This allowed the estimation of activation energies of flux and permeance. With the help of empirical correlations it was possible to estimate activations energies of diffusion and sorption. Comparing these activation energies and using different solubility parameters several conclusions were obtained: flux was activated by temperature except for MEOH in [OMIm][Br]. Permeance was deactivated by temperature, except for DMC in [OMIm][NTf2], indicating that sorption dominates over diffusion. MEOH diffusion is faster than DMC diffusion in both ILs because of its smaller size. MEOH and DMC diffuse faster in [OMIm][NTf2] because of its lower viscosity. MEOH interaction is stronger with [OMIm][Br] than [OMIm][NTf2] due to hydrogen bonding with the [Br] anion. DMC interaction is stronger with [OMIm][NTf2] since both have more hydrophobic character than MEOH and [OMIm][Br]. Inconsistencies between the literature and the experimental results were attributed to the use of empirical correlations to estimate diffusion coefficients. Sorption test that allows the computation of sorption coefficients should be performed instead in order to obtain reliable diffusion coefficients. Regarding to the stability of these SILMs, no liquid permeate was obtained what is indicating that they are stable. However, IL was not observed in the pores of used SILM which is indicating that a large amount is removed from the pores. This could affect to their long term stability if IL is complete removed. Finally, pervaporation experiments with different binary mixtures of DMC and MEOH were carried out with SILMs containing [OMIm][NTf2], [OMIm][Br], [OMPyrr][NTf2] and [OMIm][OTf] at 30 °C. Coupling effects were observed due to interaction of MEOH and DMC while they were diffusing through the SILMs. For [OMIm][NTf2] and [OMPyrr][NTf2] similar results were obtained indicating that cation has a secondary role in solubility. The fact that permeance of MEOH and DMC was lower for [OMPyrr][NTf2] is associated with its more hydrophobic character. MEOH permeation was hindered by the presence of DMC. This can be due to a higher interaction between MEOH – DMC molecules than MEOH – IL molecules at high concentration of DMC. Low selectivity and separation factor is obtained for MEOH,

but almost pure DMC permeate is obtained at high DMC concentration. At low concentrations of DMC, MEOH drags DMC molecules increasing its permeance with respect to the pure DMC experiments. Since the azeotropic point composition of MEOH – DMC mixtures is around 30 % in weight of DMC, these SILMs do not perform well in the separation of the azeotrope. However, for GC separation since GC do not permeate in these SILMs, they could be used to increase its concentration by removing DMC and MEOH from the reaction mixture. For [OMIm][OTf], no permeate was obtained at any feed composition contradicting what was expected from the literature. This could be due to the complex MEOH – DMC – IL – supporting membrane interactions. In consequence this SILM is not appropriate for MEOH and DMC azeotropic separation either for GC purification. For [OMIm][Br] no conclusive results were obtained. To conclude, the possible causes of unexpected behaviours in SILM permeance were discussed indicating that a chemical reaction at higher temperatures or the absorption of atmosphere water during storage could be the reason of this phenomenon. Chemical analysis tools could be used to determine the reason of this behaviour.

To sum up, the SILMs studied in this work present very different properties depending on their cation and anion. In consequence some SILMs are useful for GC recovery while others are completely useless. More experiments based on chemical analysis tools should be performed to understand why permeance properties can suddenly change.

Appendix A

Data and Computations

A.1 Molecular weights

TABLE A.1: Molecular weight of different compounds computed using their molecular formula.

Component name	Molecular weight [<i>g/mol</i>]
MEOH	32,04
DMC	90,08
[OMIm][NTf2]	475.5
[OMIm][Br]	247.18
[OMIm][OTf]	345.401
[OMPyrr][NTf2]	478.51

A.2 Enthalpy of vaporation

For MEOH one can use the following equation [126]:

$$\Delta H_{vap} = 45.3 \exp \left(0.31 \frac{T}{T_C} \right) \left(1 - \frac{T}{T_C} \right)^{0.4241} \quad (\text{A.1})$$

Where ΔH_{vap} is in *kJ/mol* and T is in *K*. T_C is the critical temperature and it is equal to 512.6 *K*. Taking the average between the ΔH_{vap} at 30, 40 and 50 °C one obtains 36674.72 *J/mol* which is the value that is going to be used in the computations.

For DMC there is less data available in literature. Its enthalpy of vaporisation is 38.36 *kJ/mol* at 273.15 *K* [127] and 33.26 *kJ/mol* at 363.62 *K* (its boiling point) [128]. The average value is 35.8115 *kJ/mol*.

A.3 Densities

For the IL [OMIm][NTf2]:

$$\rho_{IL} = 1575.027 - 0.8544T \quad (\text{A.2})$$

Where ρ_{IL} is in *kg/m³* and T in *K*. Expression parameters were computed by linear regression of experimental data provided by Tomida et al. [129]. Valid between 293.15 and 353.15 *K*.

For the IL [HmIm][Br] that is assimilated to [OMIm][Br]:

$$\rho_{IL} = 1.437 - 0.000716T \quad (\text{A.3})$$

Where ρ_{IL} is in g/cm^3 and T in K . Expression parameters were computed by linear regression of experimental data provided by Ji-Guang et al. [130]. Valid between 293.15 and 333.15 K .

For the IL [BMPyrr][NTf2] that is assimilated to [OMPyrr][NTf2]:

$$\rho_{IL} = 1683.629 - 0.939T \quad (\text{A.4})$$

Where ρ_{IL} is in kg/m^3 and T in K . Expression parameters were computed by linear regression of experimental data provided by Gardas et al. [131]. Valid between 293.15 and 393.15 K .

For MEOH:

$$\rho_{MEOH} = 1.067 - 0.00094T \quad (\text{A.5})$$

For DMC:

$$\rho_{DMC} = 1.458 - 0.0013T \quad (\text{A.6})$$

Where both densities are in g/cm^3 and T in K . Expression parameters were computed by linear regression of experimental data provided by Rodríguez et al. [132]. Valid between 293.15 and 313.15 K .

A.4 ILs viscosity

For the IL [OMIm][NTf2]:

$$\eta_{IL} = 9.06 \times 10^{-5} \exp\left(\frac{4135.05}{T}\right) \quad (\text{A.7})$$

Where η_{IL} is in $mPas$ and T in K . Expression parameters were computed by no-linear regression of experimental data provide by Tomida et al. [129]. Valid between 293.15 and 353.15 K .

For the IL [HMIIm][Br] that is assimilated to [OMIm][Br]:

$$\eta_{IL} = 6.42 \times 10^{-8} \exp\left(\frac{7379.03}{T}\right) \quad (\text{A.8})$$

Where η_{IL} is in $mPas$ and T in K . Expression parameters were computed by no-linear regression of experimental data provide by Ji-Guang et al. [130]. Valid between 293.15 and 333.15 K .

For the IL [BMPyrr][NTf2] that is assimilated to [OMPyrr][NTf2] [133]:

$$\eta_{IL} = 9.62 \times 10^{-4} \exp\left(\frac{3351.023}{T}\right) \quad (\text{A.9})$$

Where η_{IL} is in $mPas$ and T in K . Valid between 298.15 and 353.15 K .

A.5 Saturation vapor pressure

Saturation vapour pressure of pure compounds were computed using the Antoine equation:

$$\log(P^S) = A + \frac{B}{T + C} \quad (\text{A.10})$$

Where, P^S is in kPa and T in K . Equation coefficients are presented in Table A.2, they are valid between 235–345 K for MEOH and between 273.15–548.0 K for DMC.

TABLE A.2: Antonie equation coefficients.

Component name	A	B	C
MEOH [134]	7.26415	-1615.59	-30.437
DMC [135]	6.43380	-1413.00	-44.250

A.6 Activity coefficients

Activity coefficients were computed using the NRTL (non-random two-liquid) Model. For a binary mixture of compounds 1 and 2 the equations of this model are the followings:

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \quad (\text{A.11})$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \quad (\text{A.12})$$

$$\ln G_{12} = -\alpha_{12} \tau_{12} \quad (\text{A.13})$$

$$\ln G_{21} = -\alpha_{21} \tau_{21} \quad (\text{A.14})$$

$$\tau_{12} = \frac{\Delta g_{12}}{RT} \quad (\text{A.15})$$

$$\tau_{21} = \frac{\Delta g_{21}}{RT} \quad (\text{A.16})$$

Where γ is the activity coefficient, x is the molar fraction, τ is the interaction parameter, α is the non-randomness parameter, Δg is the interaction energy parameter, R is the ideal gases constant and T is the temperature.

For the binary system containing methanol (1) and [OMIm][Cl] (2) NRTL model parameters are provided by Aznar [136]. Δg_{12} is equal to 9746.799 $J/molK$, Δg_{21} is equal to -19140.423 $J/molK$ and $\alpha_{12} = \alpha_{21}$ is equal to 0.273. For the binary mixture of methanol (1) and dimethyl carbonate (2), see Figure A.1, Δg_{12} is equal to 1575.210 $J/molK$, Δg_{21} is equal to 498.596 $J/molK$ and $\alpha_{12} = \alpha_{21}$ is equal to 0.3. These values were obtained from the software Aspen Plus® V8.0.

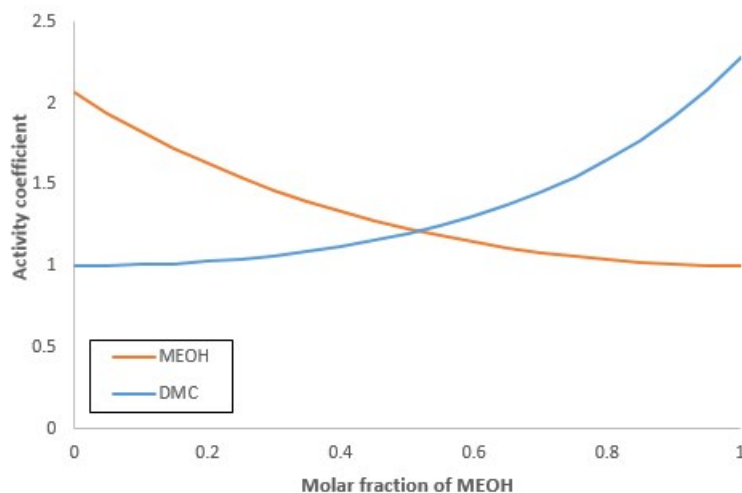


FIGURE A.1: Activity coefficients of methanol and dimethyl carbonate in a binary mixture of both components at 298.15 K.

A.7 Solubility parameters

In order to know if two substances are soluble there are several polarity scales that one can use. Here, the main scales are explained and data for MEOH, DMC and ILs are collected in order to provide a better understanding of molecular indentation between these compounds.

Hildebrand proposed the Hildebrand's solubility parameter which is computed with the following expression:

$$\delta = \sqrt{\frac{\Delta H_{vap} - RT}{V_m}} \quad (\text{A.17})$$

So this parameter is the square root of the cohesive energy density. In other words, the interaction energy between the solvent molecules [137]. As consequence, it is expected that two component with close values of their Hildebrand's solubility parameter to be soluble. Hildebrand's solubility parameters are appropriated for nonpolar and slightly polar compounds and it is limited to mixtures that provide a positive deviation from Raoul's law. Another option is the Hansen's solubility parameters which are an extension of the Hildebrand's solubility parameter to include more polar compounds. They take into account the different interactions that contribute to the cohesive energy. These interactions are dispersion forces, dipolar intermolecular forces and hydrogen bonds. In order to be soluble, two substances would have similar values of the different contributions to their cohesive energy.

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (\text{A.18})$$

Where δ_d^2 , δ_p^2 and δ_h^2 are the dispersion, electrostatic and hydrogen bonding contributions to the solubility parameter. Hildebrand and Hansen solubility of pure MEOH, pure DMC, binary mixtures of MEOH - DMC and ILs are listed in Table A.3. Some authors have reported that different techniques of computing δ in ILs can provide different results [138] [116].

The partition octanol-water coefficient, $P_{O/W}$, is the ratio of solute concentrations in octanol and water in equilibrium. It expresses how this component is going to be distributed

TABLE A.3: Hildebrand and Hansen solubility parameters in $[MPa^{0.5}]$. Values in brackets are computed using Formula A.17 and values of enthalpies of evaporation extracted from the indicated source.

Component name	δ_{Hil}	δ_{Han}	δ_d	δ_p	δ_h	T [K]	Source
[C8mim][NTf2]	25 ¹ , 24.671 ² (20)	-	-	-	-	298 ^{1,2} (298)	[139] ¹ , [138] ² ([140])
[C8mim][Cl]	17.91 ¹ , 29.051 ² (22.82)	17.62	15.25	3.10	8.24	313.15 ¹ , 298 ² (298)	[141] ¹ [138] ² ([140])
[C4mim][Otf]	25.4	-	-	-	-	298	[139]
MEOH	-	29.6	15.1	12.3	22.3		[142]
DMC	-	18.7	15.5	3.9	9.7		[142]
0.1 MEOH + 0.9 DMC	-	19.1	15.5	4.3	10.3		[142]
0.3 MEOH + 0.7 DMC	-	20.2	15.4	5.3	11.9		[142]
0.5 MEOH + 0.5 DMC	-	21.7	15.4	6.6	13.8		[142]
0.7 MEOH + 0.3 DMC	-	23.9	15.3	8.3	16.4		[142]
0.9 MEOH + 0.1 DMC	-	27.3	15.2	10.7	19.9		[142]

in both immiscible phases and it provides information about the hydrophilic - hydrophobic character of that compound. Normally the decimal logarithm of this parameter is listed in bibliography which allows a quick interpretation. If $\log P_{O/W}$ is positive or negative is indicating that a component is hydrophobic or hydrophilic. Some values are presented in Table A.4. One has to be cautious with partition coefficients values since they are concentration dependent which leads to differences between authors [143].

TABLE A.4: Octanol-water partition coefficients.

Component name	$\log P_{O/W}$	T, K	Source
[OMIm][NTf2]	0.80 - 1.04	297.15	[144]
[OMIm][Cl]	-0.27	298.15	[145]
[OMIm][Br]	-4.5	ambient	[146]
[BMIm][Otf]	-1.61	ambient	[147]
MEOH	-0.81	292.15	[148]
DMC	0.354	293.15	[149]

Finally, Kamlet-Taft solvation parameters provide information about the different contributions and interactions in solubility in a similar manner as Hansen's solubility parameters do. Kamlet-Taft solvation parameters are three complementary scales: α hydrogen bond acidity, β hydrogen bond basicity and π^* dipolarity and polarizability effects [137].

TABLE A.5: Kamlet-Taft solvation parameters computed using Reichardt's dye, N,N-diethyl-4-nitroaniline, and 4-nitroaniline and 4-nitroanisole for DMC.

Component name	α	β	π^*	Source
[BMIm][NTf2]	0.61	0.24	0.98	[150]
[OMIm][NTf2]	0.60	0.29	0.96	[107]
[BMPyrr][NTf2]	0.42	0.25	0.95	[150]
[OMPyrr][NTf2]	0.80	0.08	0.73	[151]
[HMIIm][Br]	0.45	0.74	1.09	[152]
[HMIIm][Cl]	0.48	0.94	1.02	[152]
[BMPyrr][Otf]	0.40	0.46	1.02	[150]
[BMIm][Otf]	0.62	0.49	1.00	[107]
[HMIIm][Otf]	0.67	0.52	0.98	[153]
MEOH	1.05	0.61	0.73	[150]
DMC	0	0.38	0.47	[154][137]

A.8 Mixing enthalpy

The expression of the mixing enthalpy of MEOH and [OMIm][NTf2] is available in literature [100]:

$$\Delta_{mix}H = (x - x^2)(7868 - 5596(1 - 2x) + 3763(1 - 2x)^2) \quad (\text{A.19})$$

Where $\Delta_{mix}H$ is the mixing enthalpy in J/mol and x is the molar fraction of MEOH. Figure A.2 shows the evolution of the mixing enthalpy with the composition of the binary mixture.

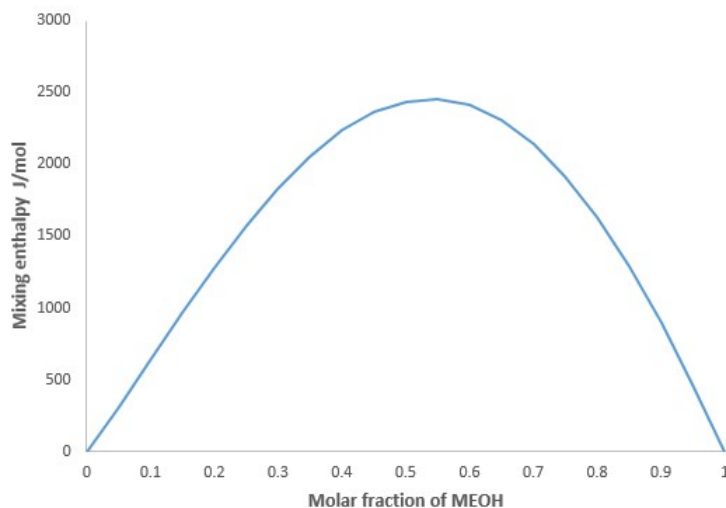


FIGURE A.2: Heat of mixing between [OMIm][NTf2] and MEOH at different binary mixture compositions.

Appendix B

Experimental measurement

B.1 Flux evolution during pure MEOH/DMC experiments

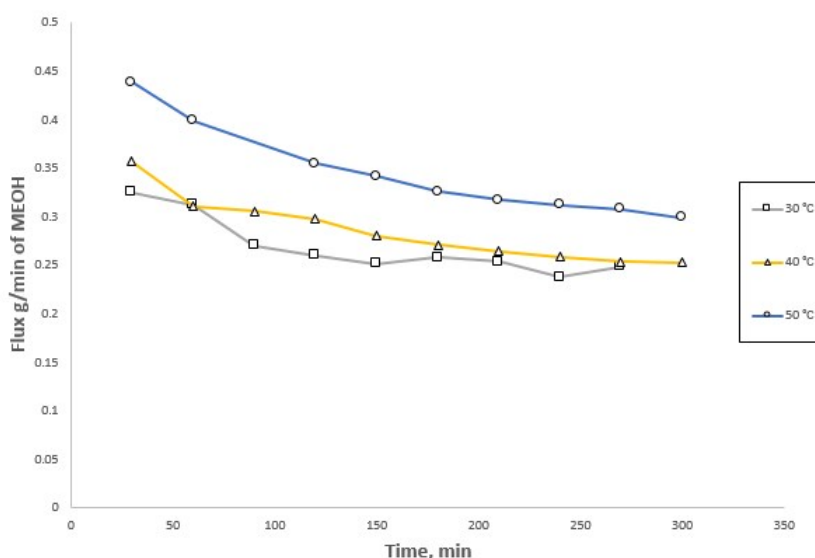


FIGURE B.1: Evolution of MEOH flux through a SILM containing [OMIm][NTf₂], prepared during 2 h at 50 mbar, at 30, 40 and 50 °C.

Pressure in the permeate side was 3 *mbar* and flow of pure MEOH between 80 and 100 *L/h*. The three experiments were performed with the same membrane. The initial weight of the SILM was 0.7549 g. This weight was reduced up to 0.4963, 0.4858, 0.474 and 0.4616 g after the 30, 40, 50 and 60 °C tests respectively. The weight of the PAN membrane was 0.4537 g.

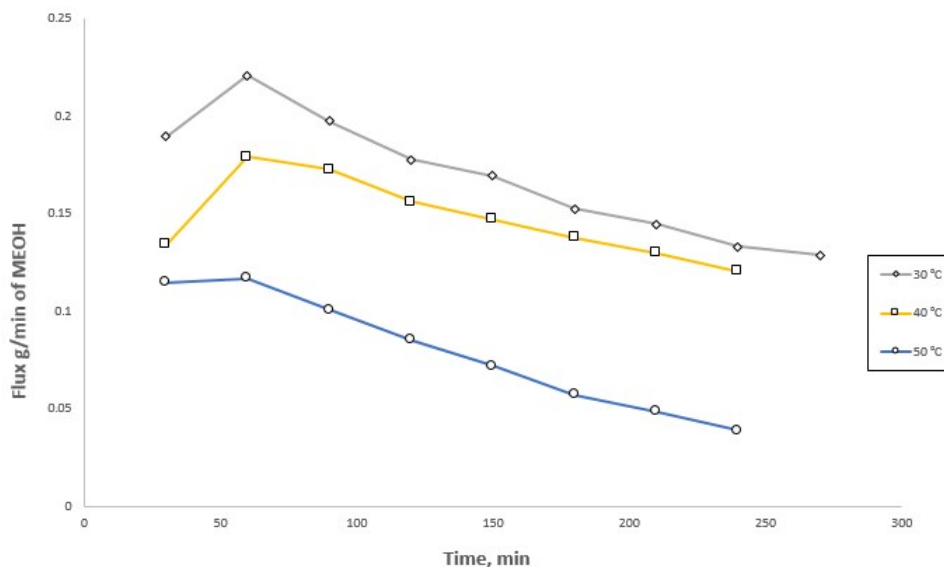


FIGURE B.2: Evolution of MEOH flux through a SILM containing [OMIm][Br], prepared during 2 h at 12 mbar, at 30, 40 and 50 °C.

Pressure in the permeate side was 4 *mbar* and flow of pure MEOH between 80 and 90 *L/h*. The three experiments were performed with the same membrane. The initial weight of the SILM was 0.6231 g. This weight was reduced up to 0.4744, 0.4753 and 0.4734 g after the 30, 40, 50 - 60 °C tests respectively. The weight of the PAN membrane was 0.4305 g.

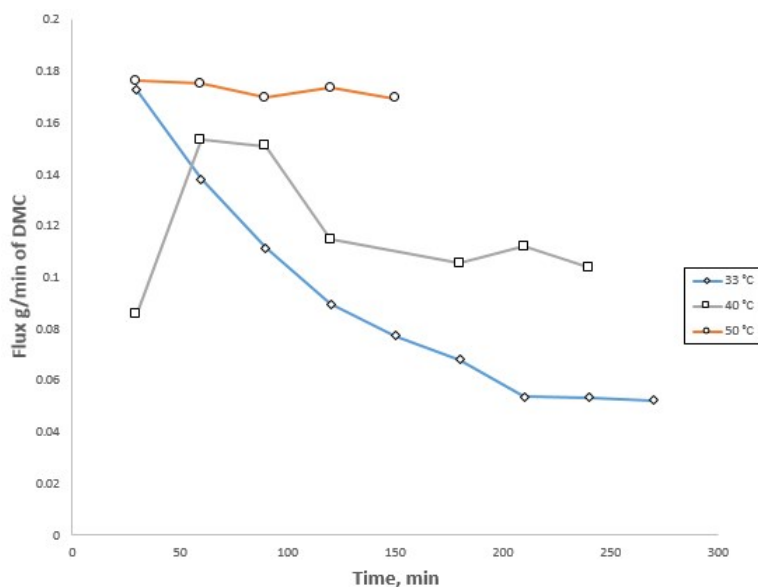


FIGURE B.3: Evolution of DMC flux through a SILM containing [OMIm][NTf2], prepared during 2 h at 50 mbar, at 30, 40 and 50 °C.

Pressure in the permeate side was 3 - 4 *mbar* and flow of pure MEOH between 80 and 90 *L/h*. The three experiments were performed with the same membrane. The initial weight of

the SILM was 0.7133 g. This weight was reduced up to 0.5506 after the 30 °C test respectively. The weight of the PAN membrane was 0.4586 g.

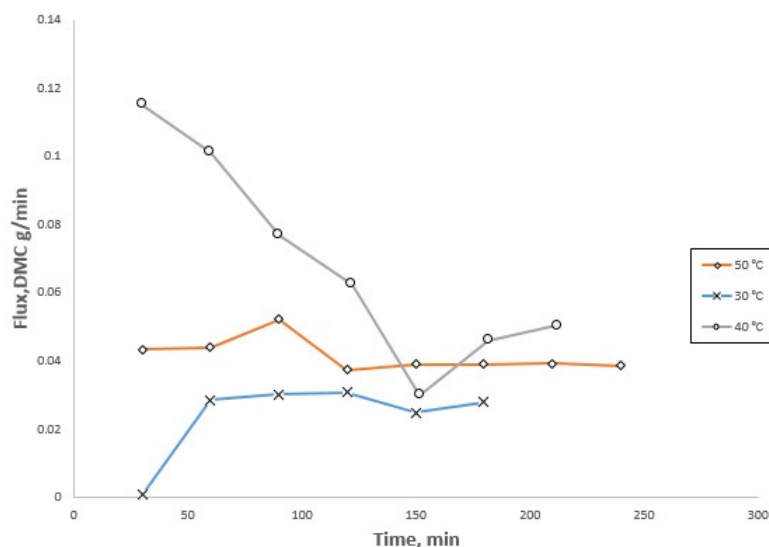


FIGURE B.4: Evolution of DMC flux through two SILM containing [OMIm][Br], prepared during 2 h at 15 or 16 mbar, at 30 (16 mbar), 40 (15 mbar) and 50 (16 mbar) °C.

Pressure in the permeate side was 1-3 mbar and flow of pure MEOH was 80 L/h. The three experiments were performed with two different membranes. The initial weight of the SILM was 0.5339 g. This weight was reduced up to 0.4436, 0.431, 0.422 g after the 50, 30 and 40 °C test respectively. The weight of the PAN membrane was 0.4106 g.

B.2 Flux evolution during binary mixture experiments

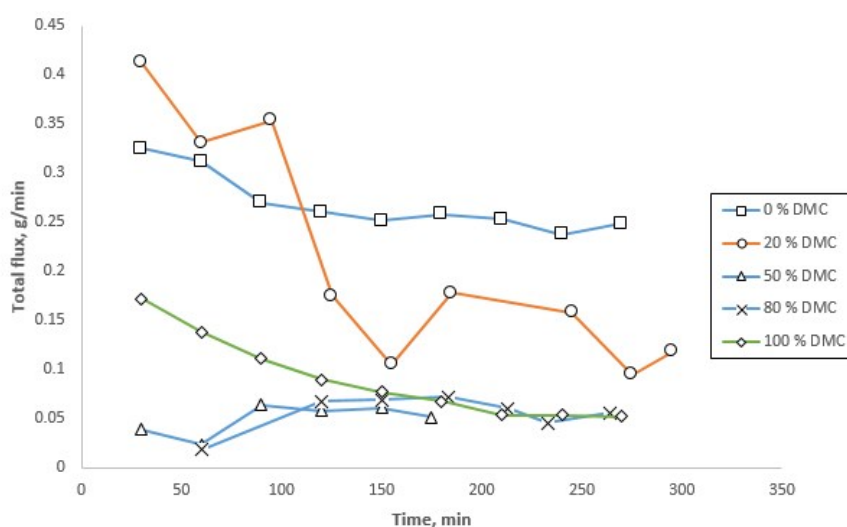


FIGURE B.5: Evolution of total flux through two SILM containing [OMIm][NTf2], prepared during 2 h at 50 mbar, at different feed compositions.

Pressure in the permeate side was 0 mbar and flow was kept between 80 and 100 L/h. The three experiments were performed with the same membrane.

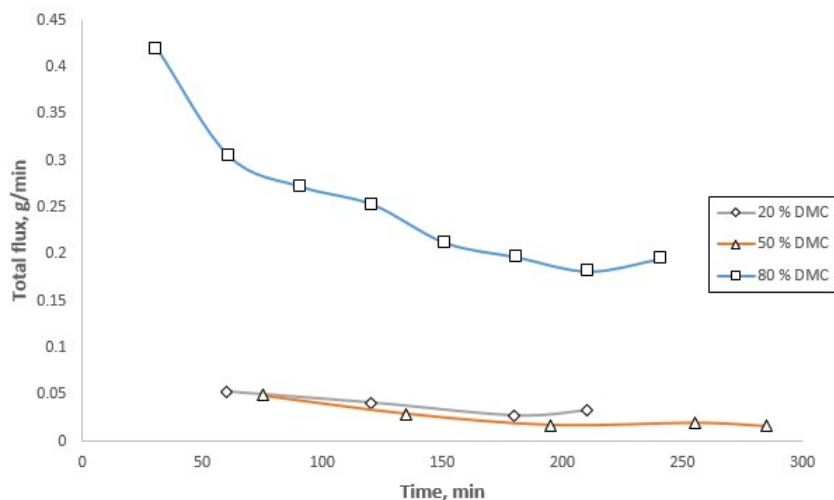


FIGURE B.6: Evolution of total flux through two SILM containing [OMPyrr][NTf2], prepared during 2 h at 50 mbar, at different feed compositions.

Pressure in the permeate side was 0 mbar and flow was kept between 80 and 100 L/h. The three experiments were performed with two different membranes.

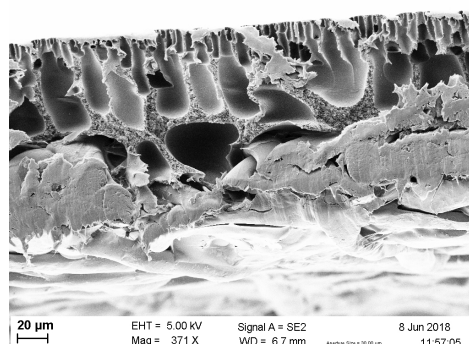
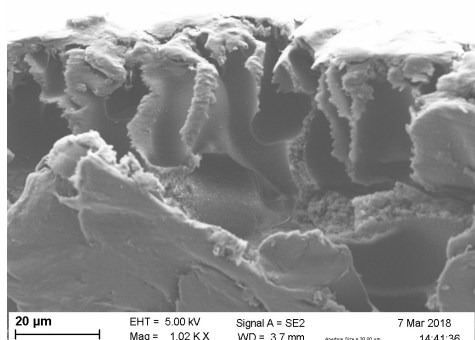
The permeate composition of every experiment measured by Gas Chromatography is presented in Table B.1.

TABLE B.1: Feed molar fraction and permeate molar fraction of DMC in the binary tests. ME OH molar fraction = 1 - DMC molar fraction.

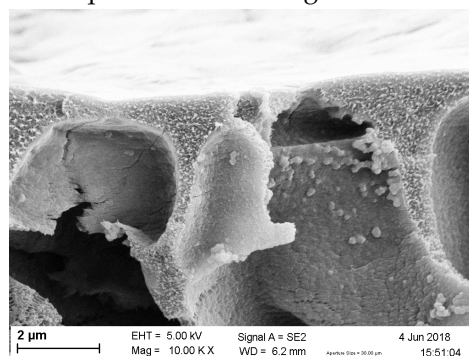
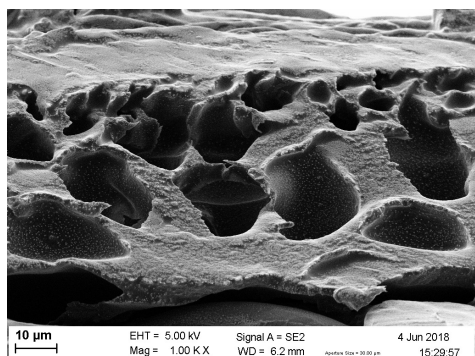
IL	Feed molar fraction	Average permeate mole fraction
[OMIm][NTf2]	0.273	0.285
	0.376	0.516
	0.698	1.000
[OMPyrr][NTf2]	0.240	0.277
	0.482	0.951
	0.813	0.978

Appendix C

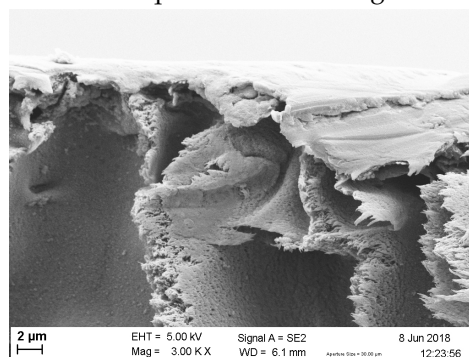
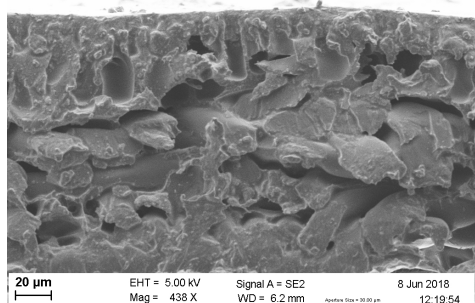
SEM images of SILM cross section



(A) Fresh PAN membrane by directly cutting with knife. (B) Fresh PAN membrane prepared by immersion in liquid N₂ and cutting with knife.

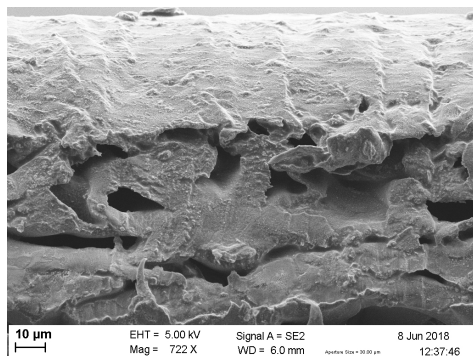


(C) Fresh SILM with [OMIm][NTf₂] prepared by immersion in liquid N₂ and cutting with knife. (D) Used SILM with [OMIm][NTf₂] prepared by immersion in liquid N₂ and cutting with knife.

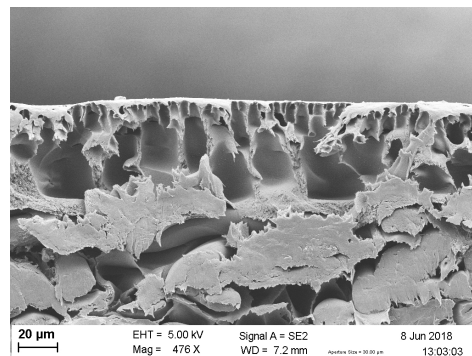


(E) Fresh SILM with [OMPyrr][NTf₂] prepared by immersion in liquid N₂ and cutting with knife. (F) Used SILM with [OMPyrr][NTf₂] prepared by immersion in liquid N₂ and cutting with knife.

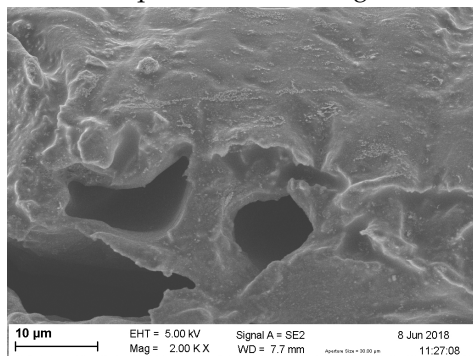
FIGURE C.1: SEM images of SILMs cross sections.



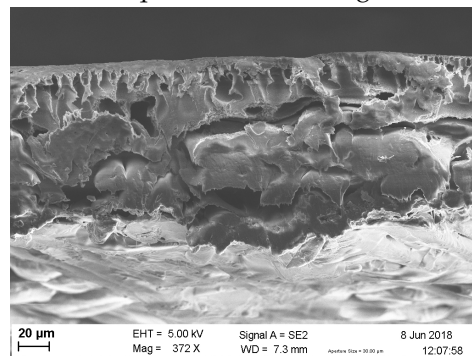
(A) New SILM with [OMIm][OTf] prepared by immersion in liquid N₂ and cutting with knife.



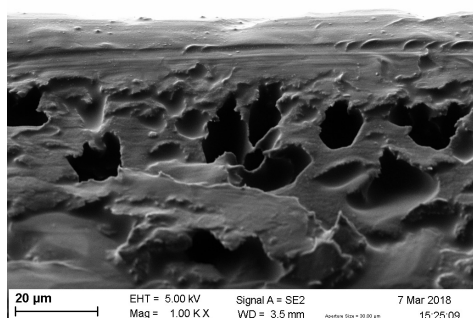
(B) Used SILM with [OMIm][OTf] prepared by immersion in liquid N₂ and cutting with knife.



(C) New SILM with [OMIm][Br] prepared by immersion in liquid N₂ and cutting with knife.



(D) Used SILM with [OMIm][Br] prepared by immersion in liquid N₂ and cutting with knife.



(E) Used SILM with [P66614][Cl] prepared by immersion in liquid N₂ and cutting with knife.

FIGURE C.2: SEM images of SILMs cross sections.

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