

4 Ionic Liquid Membrane Technology

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ABSTRACT

Ionic liquids have some unique physical/chemical properties that make them excellent materials to be used in various morphologies as membranes. These morphologies include ionic liquids impregnated into the pores of supports (supported liquid membrane), polymeric versions of ionic liquids, composites of the polymer with ionic liquid, and three-component systems where there is also a solid phase such as a zeolite, and finally gelled versions. These membranes have been demonstrated for various gas and liquid phase separations. For gases, the most studied separation is CO₂ from N₂ or CH₄. Separation of organics from water is the most common liquid phase application. One additional application is as barrier materials where the membrane acts to protect against chemical warfare agents (CWAs) or other toxic chemicals while allowing water vapour to be transported. These membranes can also be used for electrochemical applications due to the ionic nature of the material.

4.1 IONIC LIQUIDS: DEFINITIONS AND PROPERTIES

Ionic liquids are molten salts composed of a bulky and asymmetric organic cation and organic or inorganic anions, which create a low lattice energy in the

crystalline structure. This structure lowers their melting point, allowing these salts to be in the liquid state at room temperature (also sometimes known as room temperature ionic liquids [RTILs]). Ionic liquids generally exhibit negligible vapour pressure [1], high thermal stability, and good solvating capacity for both organic and inorganic compounds, among many other unique properties. Given the very large number of possible ionic liquids, their properties can be fine-tuned by adequate selection of specific ions and/or functional groups, making them “tailored solvents” that can be designed to fit the requirements of a specific process.

Their unique properties allow for their application in numerous chemical and industrial processes which include chemical, catalytic, and biological reactions; organic/inorganic synthesis; separation processes; separation and purification of gases; removal of contaminants; and the replacement of conventional organic solvents. There are relevant industrial processes that use ionic liquids, such as the BASIL (Biphasic Acid Scavenging utilizing Ionic Liquids) process developed by BASF™ [2] and the Difasol process developed by the Institut Français du Pétrole, which is an improvement of the traditional Dimersol process [3].

In order to identify the best ionic liquids for a particular application, it is necessary to know their thermophysical properties and to understand the phase behaviour of the systems containing ionic liquids. This task cannot be accomplished using only the available experimental data due to the very large number of possible combinations of ionic liquids, solvents, and target solutes. It is therefore necessary to develop predictive models able to describe the behaviour of these systems, based on a few selected experimental measurements.

To model the phase behaviour, a number of excess Gibbs free energy models have been applied to mixtures containing ionic liquids and different solvents. Some classical local composition models, such as the non-random two liquid (NRTL) and UNiVersal QUAsiChemical (UNIQUAC), were also applied with success to the description of these systems [4]. The modified Flory–Huggins equation and a lattice model based on polymer-solution models have also been applied with good results [5]. Although the models employed in these studies provide good correlations, they have a very limited predictive capability since they require parameters fitted to experimental data when considering the ionic liquid complex groups. A less rigorous, but more predictive, alternative is the use of the COnductor-likeScreeningMOdel for Real Solvents (COSMO-RS), proposed by Klamt and Eckert [6], which does not require adjustable parameters being applicable to a large number of possible ionic liquids and solvents [7].

Gas solubility is one of the most important thermophysical properties when considering gas–ionic liquid systems. One approach is based on regular solution theory (RST) [8–11]. In this theory, the solubility is related to the difference in the solubility parameter for the solute and solvent squared. The solubility parameter for each component is an independent value. The

TABLE 4.1 Carbon Dioxide Solubility Data for the [C₂mim][NTf₂]-[C₂mim][BF₄] System [13]

Ionic Liquid Mixture	H_{CO_2} / atm	cm ³ gas/g IL
[C ₂ mim][NTf ₂]	50 ± 1	0.41
25 mol% [C ₂ mim][BF ₄]	58 ± 3	0.35
50 mol% [C ₂ mim][BF ₄]	65 ± 1	0.43
75 mol% [C ₂ mim][BF ₄]	85 ± 5	0.43
90 mol% [C ₂ mim][BF ₄]	91 ± 1	0.46
95 mol% [C ₂ mim][BF ₄]	94 ± 1	0.46
[C ₂ mim][BF ₄]	100 ± 2	0.50

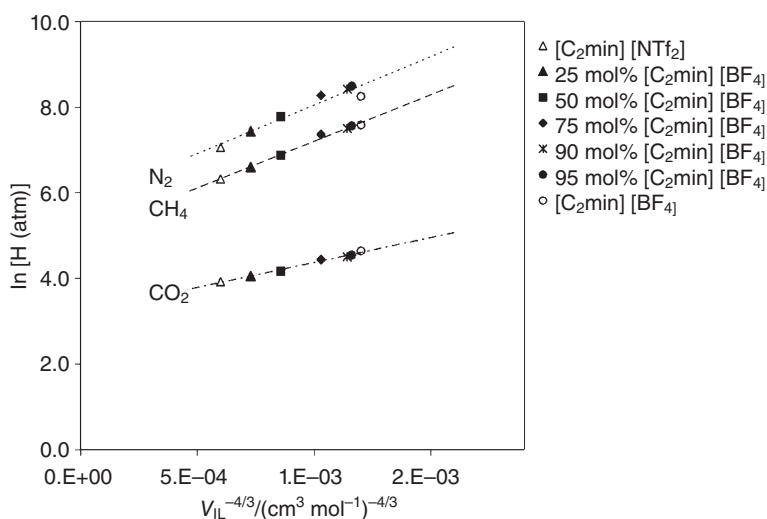


Figure 4.1 Average natural logarithm of the Henry's constant versus average measured mixture molar volume to the $-4/3$ power at 40 °C. The lines represent the RST models for each gas [13].

solubility parameters of many gases and vapours have been tabulated (Table 4.1). The temperature dependence can also be evaluated [12].

Figure 4.1 demonstrates that the RST is valid for ionic liquid mixtures. The linear relationship shows that RST can well describe the behaviour of gases in ionic liquids.

The negligible vapour pressure of ionic liquids, and the possibility to adjust and control their solubility in various solvents, make them particularly interesting for a large number of industrial processes, minimising or avoiding their loss to the environment, with the resulting economic and ecological benefits. Also, the fact that they can be designed in order to promote a high affinity to

target compounds is extremely attractive and opens perspectives for selective separation processes in the gas and liquid phases, as will be discussed in this chapter.

The integration of ionic liquids, and/or their chemistry, in synthetic membranes has been discussed since the late 1990s [14, 15]. Membranes can supply an adequate environment for ionic liquids by providing conditions for their containment and use in reduced amounts. Some properties that are usually negatively associated with ionic liquids, such as high viscosity and corrosiveness, do not represent a relevant problem if short transport paths and appropriate micro-environments are provided, respectively, as in the case in integrated membrane–ionic liquid systems. Additionally, cost issues that are also associated with some ionic liquids may be circumvented by the use of membrane systems, where a reduced amount of ionic liquid is employed and, in many cases, under regenerative conditions.

Although commonly regarded as “green solvents,” many ionic liquids described in the literature and used in numerous processes have been characterised as toxic to humans and other biological entities [16, 17]. In many cases, the “green character” of ionic liquids results mostly from their ease of confinement due to their negligible volatility and adjustable solubility. Membrane confinement can contribute significantly to reinforce their sustainable use.

4.2 STRUCTURE AND MORPHOLOGY OF IONIC LIQUID MEMBRANES

Ionic liquids can be used in various morphologies or configurations as membranes. Three intrinsic properties of ionic liquids that differentiate them from common organic solvents and water are non-volatility, thermal stability, and tuneable chemistry. These characteristics make ionic liquid membranes promising in industrial applications, particularly in gas (i.e., CO₂) separation and sequestration. The incorporation of these ionic liquids in a membrane can improve membrane separation performance, adding increased “liquid-like” gas solubility behaviour to the membrane. In addition, the ionic liquid can be functionalised to provide increased solubility and selectivity.

4.2.1 Supported Liquid Membranes (SLMs) and Contactors

Membrane contactors are devices that promote the non-dispersive contact between two different phases (gas–liquid or liquid–liquid) in order assure a high interfacial area for mass and heat transfer [18, 19]. The membranes may be porous or non-porous. In this section, we will focus our attention on porous membrane contactors that separate two different phases. The transport of target solutes from a feed to a receiving stream takes place through the pores of the membrane, which are wetted by the phase with the highest affinity towards the membrane (hydrophobic–hydrophobic or hydrophilic–hydrophilic

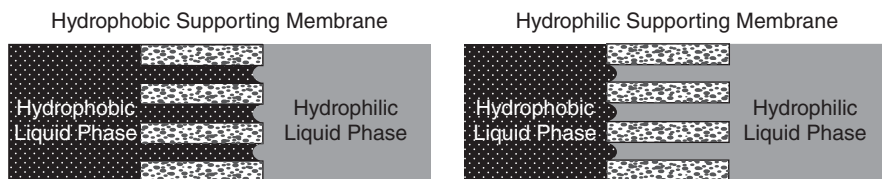


Figure 4.2 Wetting of contactor membranes according with hydrophobic–hydrophobic or hydrophilic–hydrophilic affinity.

TABLE 4.2 Specific Area of Contact of Mass Transfer Equipment

Equipment	Specific Area/m ⁻¹
Settler/decanter	3–30
Plate and packing columns	30–300
Rotating disc columns	150–500
Membrane contactors	1500–7000

affinity). Figure 4.2 shows a scheme of a hollow fibre membrane contactor, where the hydrophobic membranes are preferentially wetted by a hydrophobic solvent, and the opposite situation where a hydrophilic membrane contactor wetted by a hydrophilic liquid phase.

This equipment has several important advantages over conventional equipment used for mass transfer processes, such as a very high specific interfacial area (up to $\sim 7000 \text{ m}^2 \text{ m}^{-3}$, see Table 4.2 for comparison with traditional equipment), which translates into high mass transfer rates, and no risk of phase dispersion if an appropriate pressure difference is adjusted between the two sides of the membrane. This avoids the need for subsequent phase separation and has a number of additional advantages in terms of fluid selection (no need for a density difference between the two phases) and operating conditions (no risk of flooding or short circuiting).

Both polymeric and ceramic membranes may be used, based on the required conditions in terms of chemical and thermal stability. This equipment has been progressively adopted in industrial and medical applications for gas absorption and stripping, gas humidification and drying, and liquid–liquid extraction [20].

The concept of a membrane contactor has been extended to the development of SLMs where a selected solvent is immobilised and retained inside the porous structure of the membrane material by capillary forces. In this case, an integrated absorption/stripping process can take place in the same equipment unit, which also applies to integrated extraction/re-extraction (see Fig. 4.3). This configuration is particularly attractive because very small amounts of solvent are required within the porous structure and because the solvent is

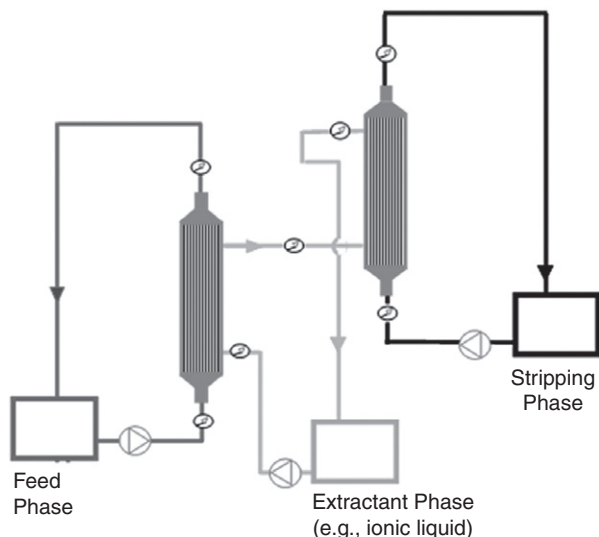


Figure 4.3 Diagram of membrane contactor integrated extraction/re-extraction system.

continuously “regenerated” when using the integrated absorption/stripping or extraction/re-extraction approach. Additionally, the transport path through the immobilised solvent phase can be greatly reduced to a few micrometres, when compared with the situation of transport in a typical membrane contactor where transport through the bulk solvent phase also has to be considered.

The assembly and operation of membrane contactors in bench and industrial scales is relatively simple but the preparation of SLMs, although simple on a laboratory scale [21–23], still remains a technical challenge for large-scale applications.

The major drawback of membrane contactors and SLMs is the fact that most solvents are volatile and/or may be solubilised in the contacting phase(s). These features translate into a loss of solvent, with consequent failure of stability and selectivity, and contamination of the contacting phase(s). Due to their extremely low volatility, ionic liquids represent an interesting alternative, assuring no solvent loss during operation of gas–liquid processes. If liquid–liquid systems are considered, ionic liquids may also be applied advantageously through modulation of their solubility in the contacting liquid phases, by judicious selection of their cation and anion constituents.

The use of membrane contactors and SLM systems employing ionic liquids has been widely reported in the literature for gas and vapour absorption, where feed streams containing target solutes are processed with ionic liquids that exhibit high selectivity and good chemical and thermal stability. The recent development of task-specific ionic liquids [24], notably CO₂ task-specific

ionic liquids [25], opens very interesting perspectives for selective gas and vapour transport and capture. The good thermal stability of many ionic liquids at temperatures of up to $\sim 250^\circ\text{C}$ opens also the possibility for operation at process temperatures, with the corresponding advantages in terms of mass transport rates, process simplicity, and economy.

Room temperature ionic liquids on a micro-porous support have shown promising CO_2 separation performance in the laboratory. Various 1-alkyl-3-methylimidazolium ionic liquids on a micro-porous support or substrate exhibit CO_2 permeabilities of 1000 Barrers with a CO_2/N_2 selectivity of 21. However, when the pressure drop across the membrane exceeds values as low as 2 atm, the liquid is dislodged from the membrane, destroying its functionality [26].

Research at the University of Colorado has demonstrated that SILMs containing ionic liquids (SILMs) can be prepared and used for gas separations. Relatively stable SILMs can be made by impregnating commercially available micro-porous hydrophilic polymeric (polyethersulfone [PES]) or ceramic (Alumina Anodisc®) substrates. Various ionic liquids such as $[\text{C}_2\text{mim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$, $[\text{C}_2\text{mim}][\text{CF}_3\text{SO}_3]$, $[\text{C}_2\text{mim}][\text{N}(\text{CN})_2]$, $[\text{P}_{6,6,14}]\text{Cl}$, and $[\text{C}_6\text{mim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ were used to prepare these SILMs, which exhibited a combination of high permeability and selectivity for carbon dioxide.

Another type of supported membrane involves incorporation of ionic liquids into a conventional polymer membrane [27–29]. In this configuration, the material will maintain the solubility selectivity while enhancing the diffusion rate across the membrane since the material now has more liquid-like behaviour. The ionic liquid is contained in the membrane due to the strong electrostatic interactions with both the liquid and the ionic polymer. The development of systems for separation of mixed gases and removal/recovery of vapours will be addressed in detail later in this chapter.

With the use of membrane contactors, and SILMs for liquid–liquid contact and transport, the challenge remains in finding the adequate compromise between highly selective systems for target solutes, while assuring no loss of the ionic liquid phase to the contacting phase(s). Successful applications for solute transport between organic solvent phases and ionic liquid phases have been reported [30], although transport between an aqueous phase and an ionic liquid phase is more problematic, even when the solubility of the ionic liquid in aqueous media is extremely reduced, due to the progressive formation of aqueous microdomains inside the ionic liquid phase, leading to an incremental loss of selectivity and stability [31, 23]. Separations in the liquid phase will be also discussed in detail later in this chapter.

4.2.2 Polymer Ionic Liquid Membranes

4.2.2.1 Ionic Liquid as a Polymerised Membrane (poly[RTILs]). Room temperature ionic liquids (RTILs) can be made in a polymer form. If the cation contains a polymerisable group, it can be readily converted into solid, dense

polymers—poly(RTILs)—for use as gas separation membranes [32]. The cation can be readily functionalised to incorporate unsaturated carbon-carbon bonds that can form polymers [32, 33] to be used as a membrane. This configuration eliminates the issues of ionic liquid displacement due to a pressure gradient, as in the case of a SILM using a solid micro-porous support where the liquid is held in the pores by relatively weak capillary forces.

The cation-anion constituents of a polymerised ionic liquid can be varied to achieve an application-specific performance, a so-called tuning of the RTIL membrane to be task specific. Bara et al. [32] synthesised and converted a series of ionic liquid monomers with varying length of *N*-alkyl substituents to form polymer films. These membranes were tested for their performance in separations involving CO₂, N₂, and CH₄. The CO₂ permeability was observed to rise in a non-linear fashion as the *N*-alkyl substituent was increased. Specific performance differences will be discussed in more detail in a subsequent discussion of gas separation using RTIL membranes.

Poly(RTILs) are now a reality (see Figure 4.4). Imidazolium materials are versatile building blocks, with modular or “snap together” chemistry, which allows for the incorporation of a wide variety of functional groups in the RTILs. Imidazolium cations have been tailored to form “task-specific” ionic liquids for gas separations and other applications [25, 32, 34].

Cross-linkable gemini RTILs (GRTILs) have been synthesised into thin film polymer sheet membranes, poly(GRTILs) [33]. These membranes were found to have relatively low permeability to various gas constituents—CO₂, N₂, CH₄, and H₂—when compared to other poly(RTIL) membranes, due to highly restricted diffusion through the membrane’s more contorted molecular structure. These membranes have a potential application as barriers, preventing the transport of a given gas constituent. Such an application would be in protective garment materials for protection against hazardous vapours such as CWAs and toxic industrial chemicals (TICs). As with other RTIL membranes, these could be “tuned” to a specific task or application.

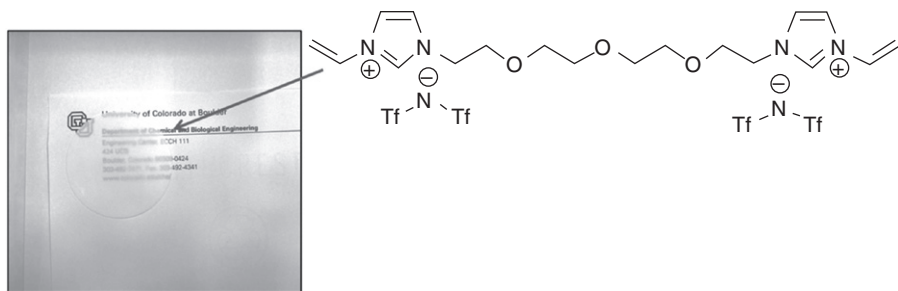


Figure 4.4 A semi-transparent disc of a poly(RTIL), containing no free ionic liquid, prepared from the illustrated vinylimidazolium ionic liquid on a polyethersulfone (PES) support.

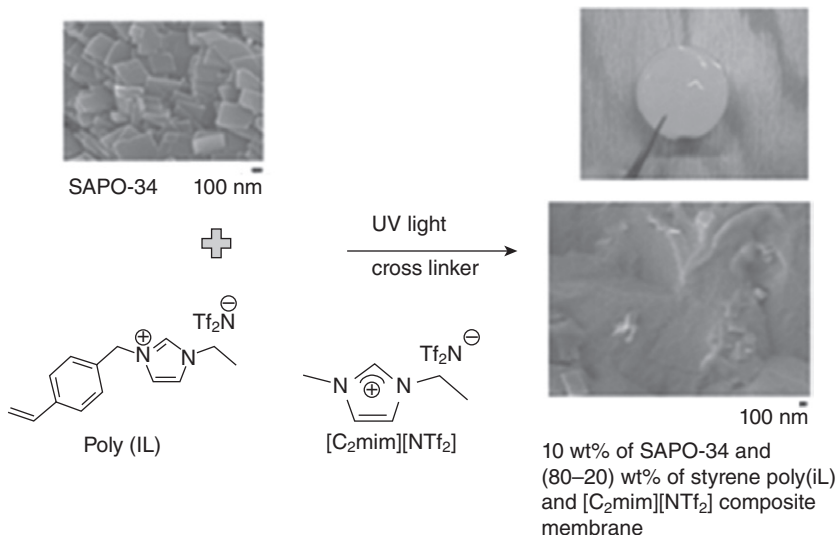


Figure 4.5 A typical three-component mixed-matrix membrane (MMM) [36].

4.2.2.2 Three-Component Composite Membranes (MMMs). More recently, a three-component MMM has been developed that alleviates the problem associated with a lack of adhesion between the polymer and the solid phase (Figure 4.5). Free ionic liquid is added to the material that wets both the polymer and the solid. This wetting phase provides a selective layer between the solid and polymer. Since the IL is non-volatile, it remains in the membrane (see, for example, Figure 4.6) [35, 36]. The three components of a composite membrane are a poly(RTIL), a free RTIL, and a micro-porous solid, such as a zeolite. This is also referred to as an MMM.

4.2.3 Gelled Ionic Liquids

A recent morphology advancement is the formation of composite liquid-polymer structures [27, 29]. These materials have improved mechanical properties in comparison with the liquid (in an SLM), but improved diffusion properties compared with the polymer phase. This structure is achieved by the blending of a “free” ionic liquid with poly(RTILs) to form a homogeneous composite membrane. Technically, this is a composite membrane. However, with enough free ionic liquid, it can be considered as a gelled membrane.

Voss et al. [37] fabricated and analysed the performance of a true gelled RTIL, 1-hexyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)amide, [C₆mim][NTf₂]. The gelled RTIL is produced using the low molecular weight gelator (LMOG), 12-hydroxystearic acid. Here the gelled structure is a gelled RTIL with no poly(RTIL) (see Fig. 4.7).

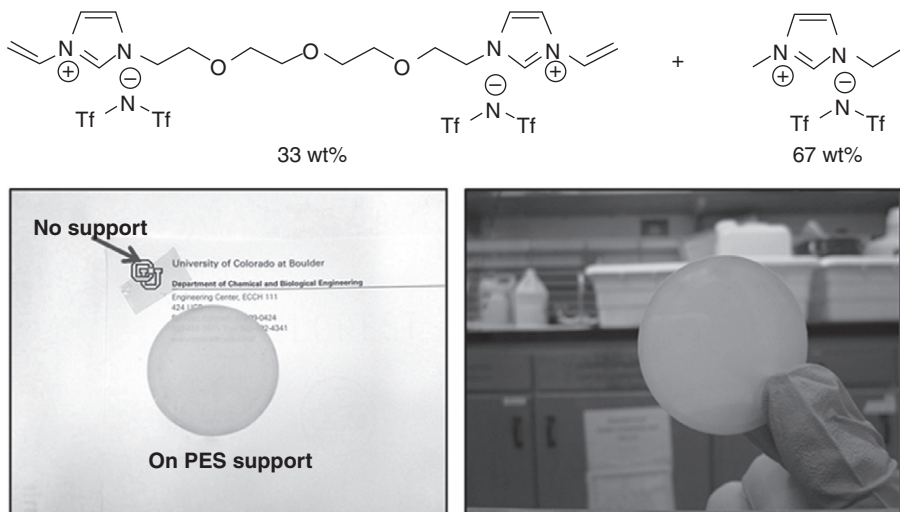


Figure 4.6 A composite of a poly(RTIL) with incorporated free [C₂mim][NTf₂], supported on a polyethersulfone (PES) support.

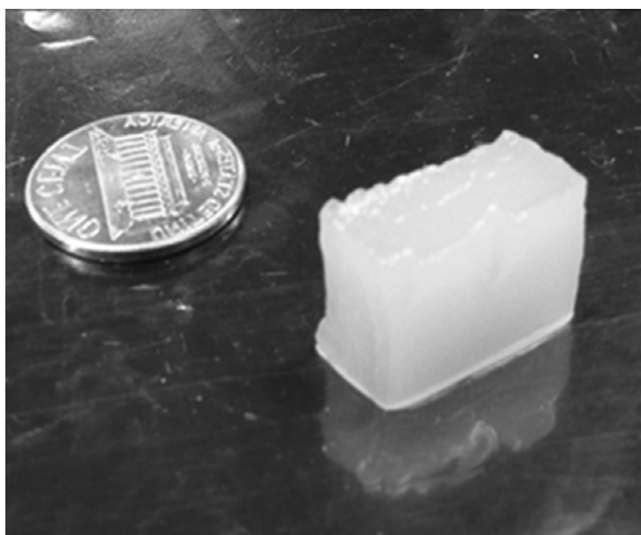


Figure 4.7 A photograph of a gelled RTIL [37].

The gel would normally require a support since it is not as mechanically stable as a regular polymer film membrane, such as poly(RTIL). The preparation procedure is independent of how it would be used.

4.3 CHARACTERISATION OF IONIC LIQUID MEMBRANES

The characterisation of ionic liquids is widely discussed in the literature covering all relevant aspects, from purity issues, structural aspects, thermodynamic, thermophysical and transport properties, electrical and optical properties, and ecotoxicity. The variety of techniques used for such extensive characterisation include, in a non-exhaustive list, elemental analysis, nuclear magnetic resonance (NMR), mass spectrometry, Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) techniques, small-angle X-ray scattering, thermogravimetry and calorimetry, conductivity, cyclic voltammetry and impedance spectroscopy, rheology studies, and toxicity evaluation with various *in situ* and *in vivo* model systems [38–40].

A detailed presentation and discussion of these studies is outside the scope of this chapter. In the following, particular attention will be given to specific techniques and studies which helped to characterise the structure and performance of ionic liquid membranes. In order to facilitate this discussion, SLMs and contactors will be examined separately from dense membranes incorporating ionic liquids chemistry.

When dealing with SILMs and contactors, the first concern is the assurance of the quality of the process of ionic liquid immobilisation inside the porous membrane structure. A good immobilisation procedure implies that all pores at the membrane surface are filled with ionic liquid, assuring that no solute transport takes place through “empty” pores. The most common evaluation procedure uses a simple gas permeation test under controlled pressure difference between the feed and the downstream circuits, where the pressure increase in the downstream circuit is monitored online with a pressure transducer. A sudden increase in pressure corresponds to a situation where the transport of gas starts to take place by convective transport through unfilled pores. This simple test can determine the operating pressure difference range for a given SILM. Pressure differences of up to 2 atm can be achieved, without breakthrough, if an adequate selection of the membrane material and the immobilised ionic liquid is adopted [23].

For some gas–vapour permeation applications, this range of pressure differences may be sufficient but, for other specific applications, higher operating pressure differences are required. In those cases, the use of modified dense membranes may constitute a better approach. Stability of SLMs and contactors for liquid phase separations has been also evaluated by checking periodically the elemental composition of the membrane near its interface using XPS. By varying the incidence angle of the X-ray beam, it is possible to obtain information about the elemental composition and electronic state of the

elements at different depths (up to 10 nm) inside the membranes and know if the ionic liquid initially immobilised inside the membrane has been progressively removed [23]. Scanning electron microscopy (SEM) has been also proposed for monitoring the retention of ionic liquid within the membrane porous structure [40]. Dynamic performance tests are also essential to characterising the behaviour of ionic liquid membrane contactors and ionic liquid supported membranes. The selectivity and flux of target solutes, during operation under defined conditions, characterise the membrane behaviour and provide understanding if relevant changes in the overall membrane system (supporting membrane and ionic liquid) are taking place. This comment is also valid when studying modified dense membranes with inclusion of ionic liquids.

When dense membranes are modified by inclusion of “ionic liquid chemistry,” other complementary characterisation techniques may be used. As an example, the introduction of ionic liquid cations in proton exchange membranes such as Nafion® may be followed off-line by Raman spectroscopy [38] and online, in real time, by confocal Raman spectroscopy. This technique can provide concentration profiles of the ionic liquid cation and other compounds present across the membrane (see Figure 4.8).

The swelling behaviour of these membranes when exposed to different solvents [42], and their ability to retain solvent molecules (namely, water), under controlled temperature conditions are also relevant characteristics that have been studied by optical microscopy and thermogravimetry [41], respectively. The electrical properties of modified dense membranes with inclusion

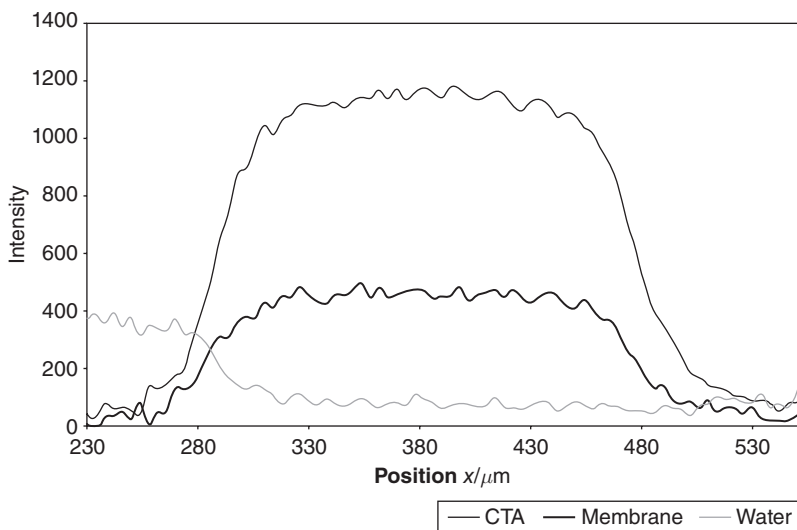


Figure 4.8 The concentration profile of $[\text{CTA}]^+$ (cetyltrimethylammonium, $[\text{N}_{11116}]^+$) and water inside a Nafion® membrane, obtained by online confocal Raman spectroscopy (unpublished data by L. Neves, I.R. Coelho, J.G. Crespo, P. Huguet, and P. Sístat).

of ionic liquid chemistry have been widely studied by impedance spectroscopy techniques, aiming at understanding the impact of introducing such chemistry on the properties of these membranes in with respect to the transport of charged species [41]. Proton mobility, as well as water structuring in these membranes, has also been studied by low-field NMR spectroscopy [43].

4.4 RECENT APPLICATIONS OF IONIC LIQUID MEMBRANES

4.4.1 Separation of Gases and Vapours: CO₂ Separation

4.4.1.1 Definitions.

4.4.1.1.1 Permeability. The permeability, P , is the product of the solubility, S , and the diffusivity, D . It is a measure of the volume flow rate of a gas per unit surface area through a membrane, normalised by the pressure gradient. It is also the product of the gas flux and membrane thickness divided by the pressure drop across the membrane. The units of permeability are Barrers, where 1 Barrer = 10^{-10} cm³ (STP) (cm cm⁻² s⁻¹ (cm Hg)⁻¹).

4.4.1.1.2 Selectivity. The separation selectivity of a membrane for a combination of gases is the ratio of the permeabilities of two gases in a mixture, P_1/P_2 . That is, then, equivalent to the ratio of the products of the solubility and diffusivity for each of the two gases, S_1D_1/S_2D_2 . It turns out that for conventional, non-RTIL polymer membranes, the selectivity is driven by the diffusion component, while for RTIL membranes (and poly(RTILs)), that selectivity is driven by the solubility component. This is due to the charged nature of the RTIL and the structure generated in poly(RTILs). RTIL “tuning” (modification of cation and or anion and alkyl group) can affect both solubility and diffusivity. The changes in diffusivity are usually minor for the polymer phase, but the solubility can change based on free volume, charge, and hydrophilic versus hydrophobic behaviour.

Solubility is obtained by measuring the gas flux through a membrane and then calculating the permeability of that gas through the membrane [44]. The permeability is determined from the measured gas flux normalised by the membrane thickness and pressure drop across the membrane. The mode of transport through the membrane is assumed to be solution diffusion, the permeability being the product of these two properties. Diffusion through the membrane can be calculated from the lag time measured before steady state is achieved in the gas flux determination [44]. The solubility is then calculated from the permeability and diffusivity.

In the case of CO₂ separations with RTIL membranes, the CO₂ solubility is enhanced over that of other gases by its quadrupole moment. The CO₂ quadrupole interacts with the charge of the ionic liquid to achieve the improved solubility and higher selectivity values with respect to other gases.

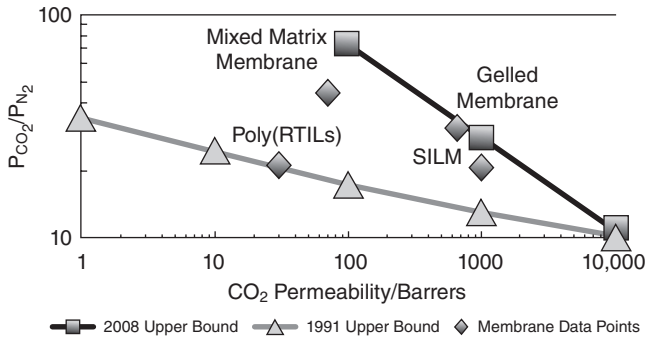


Figure 4.9 Robeson plot showing both 1991 and 2008 upper bounds.

4.4.1.1.3 Robeson Plot: A Metric for Polymer Gas Separation Membrane Performance. The Robeson plot [45] is a log–log plot of selectivity versus permeability. Specifically, it is a plot of the selectivity between two gases, P_1/P_2 , on the y-axis against the permeability of the more permeable gas, P_1 , on the x-axis. Typical non-RTIL membranes hit a so-called upper bound [46] on the Robeson plot. Currently two so-called upper bounds exist; the 1991 upper bound [45] and the 2008 upper bound [47]. The 1991 “upper bound” separates non-RTIL polymers and SLMs from membrane configurations utilising RTILs; and the 2008 upper bound defines the limit of the new RTIL-based membranes. Conventional polymer membranes used for gas separation exhibit a performance trade off. The more permeable a membrane is to a given gas, the less selective it is for that gas, and vice versa [46]. This characteristic explains the positioning of the so-called upper bounds on the Robeson plot (Figure 4.9).

4.4.1.2 CO₂ Separation. Supported ionic liquid membranes show promise in gas phase separation. Much effort is continuing in developing new SILMs for this area of application, particularly with respect to CO₂ gas separations. Industrial applications of CO₂ gas separation include natural gas sweetening, respiratory gas enrichment in life-support systems, as well as CO₂ scrubbing from power plant combustion exhaust.

Currently, the industrial methods used for CO₂ separations exact a significant energy cost, either for refrigeration in cryogenic condensation separations or regeneration of the separation medium in a bulk fluid separation, for example, aqueous amine CO₂ removal in natural gas sweetening or scrubbing of power plant flue gas.

Current CO₂ separation technology is dominated by pressure and temperature swing adsorption using liquid solvents. However, membrane-based separations have evolved and are becoming commercially viable. SILM membranes may represent an attractive, cost-effective alternative to such industrial separation applications, as the amount of material required to process the same amount of gas is greatly reduced, and regeneration process steps may be elimi-

nated. Such membranes have been used in natural gas sweetening and have been proposed for use in CO₂ capture from flue gases. RTILs present a highly versatile and tuneable platform for the development of new materials and processes aimed at the capture of CO₂ from power plant flue gas and in natural gas sweetening.

Membranes, both conventional and RTIL, have potential for separation of CO₂ from N₂ and CH₄ in industrial processes. High-throughput, highly selective polymer membranes may prove to be an alternative to amine-based CO₂ separation in natural gas sweetening [48, 49]. A small, but growing, segment of natural gas commercial sweetening operations with high CO₂ concentrations and low gas throughput do utilise polymer membranes. In applications with both high CO₂ concentration and high throughput, a combined amine-membrane process is being used.

Potential exists for polymer membranes in CO₂ capture in fossil fuel burning power plants, separating CO₂ from N₂ in the flue gas [50]. Membranes could also be used in oxycombustion, separating O₂ from N₂ in air to produce an oxygen-enriched environment in which to burn coal. The subsequent products of the combustion, CO₂ and H₂O, could be processed by condensation and CO₂ sequestration.

4.4.1.3 SILMs in CO₂ Separations. Evaluation of several different imidazolium-based RTILs revealed that SILMs fabricated with those RTILs possessed permeability and selectivity properties for CO₂/N₂ that were superior to both SLMs and conventional polymer membranes, when viewed in the context of a “Robeson plot.” Indeed, SILMs of [C₂mim][NTf₂] on a microporous support exhibited an ideal CO₂ permeability in excess of 1000 Barrers with a selectivity for CO₂/N₂ = 21 [51]. However, the SILM liquid component is still subject to displacement from the support if the pressure drop across the membrane exceeds the capillary forces or electrostatic forces holding the RTIL in its matrix.

4.4.1.4 Poly(RTILs). A possible solution to the RTIL displacement under higher differential pressure would be to formulate a polymerised RTIL-based monomer to create a poly(RTIL) [11]. Indeed, RTILs with polymerisable groups can be readily converted into solid, dense poly(RTILs) for use as gas separation membranes.

The tuneable chemistry of imidazolium-based RTILs allows for the generation of new types of CO₂-selective polymer membranes. A series of imidazolium-based RTILs bearing various length linear alkyl substituents and polymerisable units composed of a styrene or acrylate groups was evaluated [32]. By coating these monomers (mixed with a small amount of photo-initiator and cross-linker) on a porous support, and subsequent photo-polymerisation, Bara et al. formed poly(RTIL) materials as thin (~150 μm) films and studied their properties and performances relating to permeability to, and separation of, the gases CO₂, N₂, and CH₄ [32]. They measured the permeability, P , the solubility,

S , and the diffusivity, D , of the three gases for each of both styrene- and acrylate-based poly(RTILs) [32]. CO_2 permeability was observed to rise in a non-linear fashion as the alkyl substituent was increased. CO_2/N_2 separation performance was relatively unaffected as CO_2 permeability increased.

The correlation of increase in permeability of these gases through these poly(RTILs) with increasing length of the alkyl substituent may be due to the creation of more free space in the polymer, the free space being formed by an inefficient packing of the n -alkyl groups. Poly(RTILs) contain large ions, one tethered to a backbone and one free. Free space may also be generated by local repulsion between immobilised ions and so-called ion-phobic alkyl chains. It is worth noting here that poly(RTILs) differ from liquid phase RTILs in that the cations in the polymer are fixed (the anions can move very slowly), whereas there is more movement or rearrangement of ions in liquid phase RTILs.

The results from the poly(RTILs) tested by Bara et al. [32] yielded points on the Robeson plot on or slightly above that upper bound (1991 upper bound), indicating that these poly(RTILs) possess as good as or better separation properties for the gases considered (CO_2/N_2) than those of conventional, non-RTIL membranes. This is an encouraging result that should stimulate additional evaluation of new and different RTILs fabricated into poly(RTILs).

Poly(RTILs) give superior separation results for CO_2/N_2 separations when compared with conventional polymer membranes. They also perform as well as or better in CO_2/N_2 separations than their liquid RTIL counterparts containing $[\text{NTf}_2]^-$ anions [44] due to added diffusion selectivity imparted by the poly(RTIL) relative to the RTIL liquid. In addition, poly(RTILs) dissolve about twice as much CO_2 volume per cubic centimetre of material as their liquid counterpart.

4.4.1.5 MMMs in CO_2 Separation. Mixed-matrix membranes are now showing promise with respect to CO_2 separation, combining the selectivity and transport properties of inorganic membrane materials with the fabrication properties of organic polymers. Two-component solid–solid (inorganic membrane material and organic polymer) MMMs exhibit improved catalytic, optical, and electrical properties. However, such two-component membranes have limitations in light gas separation due to inadequate adhesion between the polymer and the inorganic component. This can lead to membrane failure.

In an attempt to solve this adhesion problem, or shortcoming, Hudiono et al. [35] fabricated and evaluated the light gas transport properties of a three-component composite MMM consisting of poly(RTIL), RTIL, and zeolite materials. As well as improving the adhesion of the polymer-solid membrane components, the addition of an RTIL, due to its inherent solubility and transport properties, would likely improve the gas separation properties of the membrane, making it well suited for light gas separation.

In their evaluation, Hudiono et al. prepared and tested three different composite membranes. The membrane configurations were

1. RTIL ([C₂mim][NTf₂])–zeolite
2. poly(RTIL)–zeolite
3. poly(RTIL)–RTIL ([C₂mim][NTf₂])–zeolite

Note that the zeolite used was SAPO-34, the RTIL was 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide ([C₂mim][NTf₂]), and the RTIL monomer (poly(RTIL)) was a styrene-based imidazolium RTIL monomer with methyl group substitution and [NTf₂]⁻ anions. The poly(RTIL) monomer and RTIL were chosen for their ability to absorb CO₂.

The CO₂ separation results from the three-component membrane were superior to those from the solid–solid, zeolite–poly(RTIL), membrane, CO₂ permeability going from 13.9 to 72 Barrers, and CO₂/N₂ selectivity going from 35 to 44 [34]. One drawback was a drop in CO₂/CH₄ selectivity from 35 to 30 with the three-component membrane.

The CO₂ separation results from the membranes agreed with Maxwell equation predictions involving calculations of overall conductance (permeability). This indicates that there were no defects in the fabricated membranes.

The adhesion of the RTIL to both the polymer and inorganic zeolite was also investigated using electron microscopy and contact angle measurement. The work of adhesion, the work per unit area required to separate two materials, was calculated using contact angle, surface tension, and the Young–Dupre equation.

Hudiono et al. [35] concluded that the RTIL addition improves the structural integrity of the membrane by its action as a wetting agent to improve the interfacial adhesion between the poly(RTIL) and the inorganic zeolite. The charged nature of the RTIL may also contribute to that improved interfacial adhesion/interaction.

This improved interfacial adhesion and improved CO₂/N₂ selectivity indicate that such a three-component composite membrane would be viable for gas separations, increasing the mechanical stability of the membrane. It is also likely that, by altering the relative amounts of zeolite and RTIL in this three-component configuration, additional separation performance could be achieved. Additional performance improvement might also come from selection of different RTILs.

4.4.1.6 Gelled Membranes in CO₂ Separation. Supported liquid membranes possess superior transport properties compared with solid polymer membranes, as the diffusivity in the liquid is greater than that in the polymer. However, those liquid membranes are subject to loss due to evaporation into the gas phase as well as displacement or the liquid phase by differential pressures. Use of RTILs in SLMs eliminates the loss due to evaporation, having a negligible vapour pressure. The use of the RTIL in an SLM preserves the superior liquid transport properties.

However, the problem of RTIL displacement due to pressure differential remains. This mechanical deficiency can be overcome by use of a gelled

membrane structure. The gelled membrane is a blend of free liquid RTIL and poly(RTIL) to form a homogeneous composite or gelled membrane [34]. This provides improved mechanical stability over the supported liquid option while retaining much of the performance of the SLM. Technically, this is a composite membrane, but as the liquid portion increases it becomes a gelled structure. The inclusion of the free liquid RTIL provides increased diffusivity in this gelled configuration. Effectively, the gelled membrane provides a solid polymer-like membrane structure with liquid-like gas transport.

Voss et al. [37] fabricated and tested a gelled membrane for CO₂ gas separation and compared the results obtained with other membrane configurations. They used an imidazolium-based RTIL, [C₆mim][NTf₂], in their work [37]. The gel was fabricated using an LMOG (12-hydroxystearic acid). In general, imidazolium-based RTILs have excellent solubility and solubility selectivity for CO₂ over N₂. The gelled RTIL membrane yielded gas separation performance properties on a par with those obtained from a “neat” RTIL membrane (a supported RTIL membrane). The CO₂ gas permeabilities obtained were 650 Barrers for the gelled membrane and 700 Barrers for the neat RTIL SILM. Selectivities for CO₂/N₂ were 31 and 33, respectively, for the gel and the neat SILM, where “neat” refers to a pure liquid RTIL.

This is a significant result in that it demonstrates that the gas separation properties of the gel are nearly as good as those of the supported RTIL membrane, and possess superior mechanical properties. In addition, these results are similar to results for other RTIL membrane configurations that are potentially viable candidates for industrial gas separations.

4.4.2 Barrier Materials

Currently, protective garment materials for protection against hazardous vapours such as CWAs and TICs are either dense, completely impermeable polymers (i.e., cross-linked butyl rubber) or composite membrane systems that rely on an active sorbent, such as activated carbon, to remove hazardous penetrants. The first type of protective material quickly generates heat stress in the wearer because evaporative cooling is blocked, and the second type is often bulky, heavy, and has a limited capacity and shelf life.

New functionalised poly(RTIL) composite membrane materials that allow facile water vapour transport for evaporative cooling while completely blocking the transport of the blister CWA simulant, CEES (2-chloroethyl ethyl sulfide; C₂H₅SCH₂CH₂Cl), have recently been reported. The first system is based on a new hydrophilic poly(diol-RTIL) that readily transports water vapour [52], blended with a commercial organic amine or copolymerised with an amine-containing co-monomer. For example, an approximately 150- μ m-thick film of a 9:1 composite of poly(diol-RTIL)/*N,N,N',N'*-tetramethylhexane-1,6-diamine, Figure 4.12(a), was found to exhibit a water vapour flux at room temperature of 3770 g m⁻²·day while completely blocking CEES vapour transport. The desired water vapour flux for military protective garments is 1500–

2000 g m⁻²·day⁻¹ [53]. In comparison, a pure poly(diol-RTIL) film of the same approximate thickness, but without added amine, shows a water vapour flux of 6200 g m⁻²·day⁻¹ and 100% CEES penetration. Also, a regular non-hydroxylated poly(RTIL) film with added amine is able to completely block CEES penetration but has essentially no measurable water vapour transport.

A second system is based on the same hydrophilic poly(diol-RTIL) that exhibits high water vapour breathability, but it is blended with basic zeolite particles (e.g., Na-zeolite Y) instead of amine additives. This is the same approach as previously reported for gas separations [34]. An approximately 150- μ m-thick film of this material containing 20 wt% Na-zeolite Y was found to have a water vapour flux of 2870 g m⁻²·day⁻¹, while completely blocking CEES vapour transport. Mechanistic studies on these two breathable poly(RTIL) composite systems for blister agent (i.e., mustard gas (HD); bis(2-chloroethyl)sulfide; S(CH₂CH₂Cl)₂) protection are currently in progress with CEES, in order to determine their mechanisms of action.

Bara et al. [33] reported permeability results from membranes fabricated from cross-linked GRTILs. They found that the permeabilities to the gases CO₂, N₂, CH₄, and H₂ were much lower when compared with previously studied poly(RTIL) membranes. They concluded that further investigation of these types of membranes was warranted for possible application in barrier materials.

4.4.3 Separations in the Liquid Phase

Considering the possibility of designing extremely hydrophobic ionic liquids, such as imidazolium-based ionic liquids with long alkyl side chains (e.g., [C₈mim]⁺-based ionic liquids), the potential use of these ionic liquids in aqueous/IL membrane contactors and/or aqueous/IL/aqueous SLMs seemed rather attractive. Actually this, and other hydrophobic ionic liquids, proved to be rather selective for the extraction of target hydrophobic solutes from aqueous media, such as esters of amino acids and other organic compounds [15, 54, 40]. When these ionic liquids were tested in SILMs, for integrated extraction/re-extraction of hydrophobic solutes from/to aqueous environments, the initial target solute selectivity was observed to decrease progressively until there was a total loss of selectivity. This disappointing behaviour was understood when transport studies using tritiated water, added to the feed compartment, demonstrated clearly that water transport occurs between the two aqueous compartments through the hydrophobic ionic liquid. This behaviour was also confirmed by the transport of sodium chloride, insoluble in very hydrophobic ionic liquids, whose transport through this type of SILMs was explained assuming that water clusters develop inside the hydrophobic ionic liquid, providing the necessary micro-environment for solubilising sodium chloride. The formation of dynamic water clusters inside ionic liquids was also confirmed experimentally and by recent dynamic simulation studies.

As a consequence of this behaviour, the practical application of SILMs for solute recovery from aqueous environments is limited, although several strategies have been developed in order to hinder and retard the development of water clusters inside the ionic liquid phase. In situations where a prolonged operation is not required, it may be possible, by using these methodologies, to operate during a time window where a desirable selectivity is maintained [42].

This behaviour under the presence of water also raises important questions when operating with vapour streams containing a non-negligible amount of water vapour. Under these circumstances, strategies for controlling the presence of water vapour in the vapour phase have to be taken into consideration. In specific cases, the ability to develop water clusters inside ionic liquids, even if they are extremely hydrophobic, may have an advantage. This is the case of enzymatic catalysis in ionic liquids, where a controlled water activity inside the ionic liquid is necessary in order to assure an optimal enzyme conformation and corresponding activity and selectivity.

The use of ionic liquid membrane contactors and SILMs for solute recovery and transport from/to organic solvents has revealed to be less prone to stability problems. A large number of successful applications have been referred to in the literature for the selective recovery of target solutes from organic media, their transport through the ionic liquid phase, and recovery in a receiving organic media. One of the first applications described in the literature [15] refers to the resolution of the isomeric amines diisopropylamine (DIIPA) and triethylamine (TEA), which were continuously fractionated over two weeks without any observable decrease in selectivity, using a SLM that contained the RTIL 1-butyl-3-methylimidazolium hexafluorophosphate immobilised in the porous structure of a hydrophilic polyvinylidene fluoride membrane. A higher affinity and transport rate was observed for the secondary amine, which establishes stronger hydrogen bonding with the imidazolium cation. The reason for a stronger hydrogen bonding for the secondary amine DIIPA over that for the tertiary amine TEA may be attributed to the combination of the effect of the higher basicity of DIIPA ($pK_b = 2.95$), over that of TEA ($pK_b = 3.35$), and the steric hindrance of TEA observed on formation of the H-C(2) hydrogen bonding with the imidazolium cation (see Figure 4.10).

These studies demonstrate the feasibility of using ionic liquids as a new kind of solvent in SLMs for selective transport of organic molecules. Systematic experiments have been performed and reported in the literature [55–58] with different mixtures of compounds with representative organic functional groups. From these results, it can be concluded that the appropriate combination of selected ionic liquids and supporting membranes is crucial for achieving good selectivity in a given separation problem.

The emergence of new ionic liquids and the high variety of commercial supporting membranes will enable the design of IL/supporting membrane systems that allow one to obtain the desired selectivity for a specific substrate mixture. The high selectivity obtained for the separation of mixtures with very

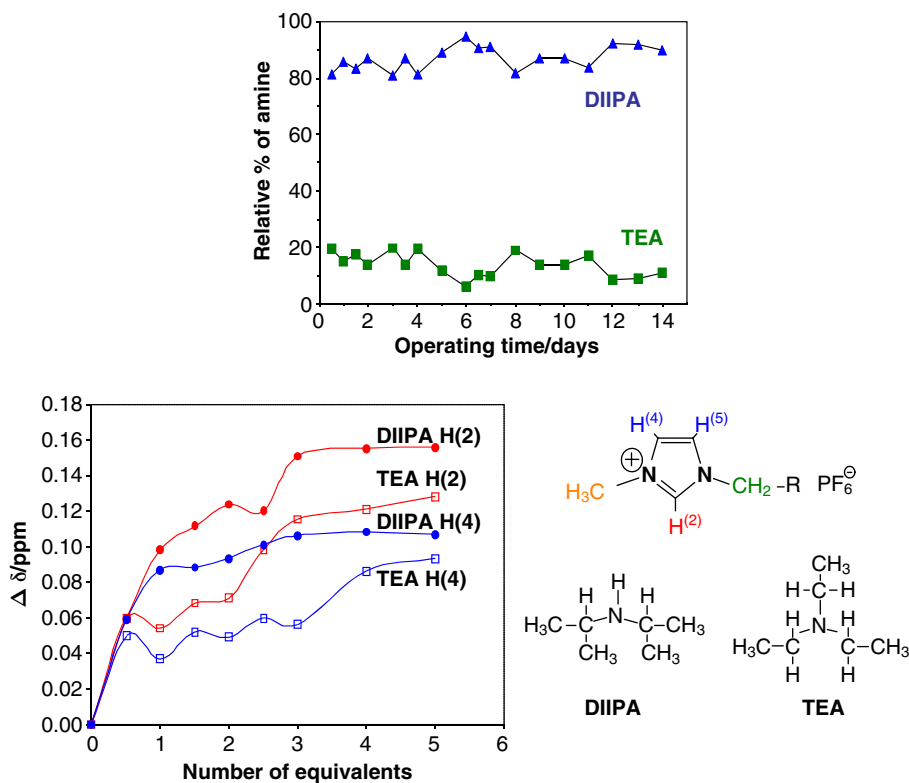


Figure 4.10 Selective transport of diisopropylamine (DIIPA) over triethylamine (TEA), using a 1-butyl-3-methylimidazolium hexafluorophosphate SLM.

similar boiling points demonstrates the potential for the use of this methodology for continuous separation of compounds from complex mixtures, namely separations difficult to achieve by using traditional distillation methods.

Finally, it is also worth mentioning the integration of catalysis in ionic liquid media with membrane processing, for catalyst and solvent reuse. Actually, the post-reaction separation of ionic liquids and catalysts from reaction products is an unresolved challenge in the application of ionic liquids to organometallic catalysis. Recent reports [59–61] addressed this challenge using organic solvent nanofiltration technology. As an example [62], Suzuki reactions were carried out in a homogeneous solution, comprising 50:50 wt% ethyl ethanoate and ionic liquid. The post-reaction mixture was diluted further with ethyl ethanoate and then separated by nanofiltration into a permeate fraction and a retained (retentate) fraction. The product was recovered in the nanofiltration permeate, while the ionic liquid and palladium catalyst were retained by the membrane and recycled into subsequent consecutive reactions. The organic

solvent nanofiltration was able to separate the Suzuki reaction product from both catalyst and ionic liquid. All the ionic liquids screened showed positive effects on the catalytic stability, significantly reducing the formation of palladium black and providing high reaction yields over consecutive recycles.

4.4.4 Fuel Cells and Electrochemical Applications

Although polymer-electrolyte membrane (PEM) fuel cells have been known for a long time, they have not yet reached large-scale development as some issues are still unresolved. These are mainly related to limited functional characteristics of the perfluorosulfonic acid membrane electrolyte, whose conductivity relies on the level of water content. Consequently, its stability is limited to temperatures below $\sim 100^\circ\text{C}$. Proton exchange membranes that operate at temperatures above 120°C are needed to avoid catalyst poisoning, enhance electrochemical reactions, simplify the design, and reduce the cost of fuel cells. In order to design new membranes for elevated temperature operation, it is necessary to understand the chemistry, morphology, and dynamics of protons and water molecules in current membranes. Based on such fundamental understanding, membranes can be modified by controlling the polymer chemistry and architecture, or by adding inorganic fillers that can retain water under relatively low humidity conditions.

In this line of thought, Nafion® membranes have been modified by partially replacing protons for ionic liquid cations. This modification aims at promoting the water solvation of these cations, with a consequent increase in water structuring and retention even at higher operating temperatures [41]. Other approaches involve the development of anhydrous membranes based on phosphoric acid doped polymers, ionic liquid-infused polymer gels, and solid acids which enable fuel cell operation above 150°C [63, 64]. Considerable work remains to be done to identify proton transport mechanisms in novel membranes and evaluate membrane stability under real operating conditions.

This issue may be also addressed by switching to ionic liquid-based polymer membranes. Various strategies have been tested for the preparation of these membranes, including polymerisation of the components with the formation of polycations, polyanions, copolymers and special, double-ion structures, as well as blends with a neutral macromolecule, typically polyvinylidene fluoride [65]. These architectures offer a water-independent proton conductivity associated with a high thermal stability, which allows high operational temperatures, as well as basic pHs. These approaches open new possibilities in terms of catalyst design, with the ultimate goal of replacing platinum, which is impractically rare.

In this case, the proton relay molecule, instead of being H_2O , is an imidazole or an amine. The operating temperature is higher, and the environmental pH increases from 7 to 11. Neutral to basic pHs may open new possibilities in terms of catalyst design, the media being far less aggressive than the highly acidic perfluorosulfonic membrane, with the ultimate goal of replacing plati-

num [66]. The investigation of ionic liquid membranes is still in its infancy but their potential is important.

4.5 FUTURE DIRECTIONS

4.5.1 Bioreactive Systems

The literature describes a large number of studies where enzymatic catalysis was accomplished with advantage in ionic liquid media [55, 67]. As ionic liquids can be designed with different cation and anion combinations, allowing for tailoring reaction solvents with specific desired properties, they provide the opportunity to carry out many important biocatalytic reactions that are difficult to perform in traditional solvents. As compared with those observed in conventional organic solvents, the use of enzymes in ionic liquids may present significant advantages, such as high conversion rates, high enantioselectivity, better enzyme stability, as well as better recoverability and recyclability [68]. To date, a wide range of approaches has been taken to further improve the performance of enzymes in ionic liquids.

The use of enzymatic membrane reactors, where the membrane may play multiple roles—support for interface stabilisation if a biphasic system is used (membrane contactor) and support for enzyme immobilisation (or, at least, micro-environment for enzyme accommodation)—has been also widely described in the literature [69]. Identification of the best strategy for solubilising enzymes into ionic liquids while keeping or improving their, activity, selectivity, and stability remains the main challenge. Mixtures of ionic liquids with a controlled amount of water, called hydrated ionic liquids, may strongly influence the protein conformation and ultimately, its function. It is important to note that the chemical activity of water remains very low because water molecules are strongly involved in the solvation of the ions. Cholinium dihydrogenphosphate ($[\text{N}_{1,1,1,2\text{OH}}][\text{H}_2\text{PO}_4]$), composed of a chaotropic cation and a kosmotropic anion, is a typical example. Hydrated (20% water: $[\text{N}_{1,1,1,2\text{OH}}][\text{H}_2\text{PO}_4]$) was shown to be an excellent solvent for cytochrome c and other proteins. In this liquid, cytochrome c was reported to show electron transfer activity even 18 months after storage at room temperature [70]. The small amount of water provides the required hydrogen-bonding environment for the protein, assuring that it can adopt a conformation that guarantees its activity, selectivity, and stability.

Another area of research refers to the development of enzymatic fuel cells, which have already been demonstrated using aqueous electrolyte solutions. The use of ionic liquids instead of aqueous salt solutions prevents loss of enzymatic activity, as a result of the local environment that they provide [71]. Considering the large variety of substrates and enzymes available for biofuel cell applications, the use of ionic liquids as electrolytes paves the way for the development of novel bio-energy conversion systems, making biofuel cells attractive next generation energy-conversion devices.

4.5.2 Ionic Liquid Systems with Enhanced Selectivity

Since the first example of a chiral ionic liquid, 1,1-bis((2*S*)-2-methylbutyl)imidazolium bromide, containing a chiral cation, was reported in 1997 [72], the number of publications dealing with chiral ionic liquids grew rapidly and, nowadays, a large pool bearing either chiral cations or anions (but seldom both) and a wide range of functionalities is available [73]. Despite the rapid design of new chiral ionic liquids, successful applications remained hidden for some time. Actually, nine years after the original publication, the use of a chiral ionic liquid in a synthesis with an enantiomeric excess (>90%) was reported for the first time [74]. Nevertheless, this field is growing rapidly, and applications are generally divided into three different groups: chiral ionic liquids in asymmetric synthesis, spectroscopic applications of chiral ionic liquids, and chromatographic applications of chiral ionic liquids.

The combination of chiral ionic liquids with membranes has been scarcely reported in the literature although the potential for its use has been recognised [75]. Developments achieved with chiral ionic liquids as stationary phases for gas chromatography may be adapted with advantage using membrane contactor technology. Ephedrinium-based* chiral ionic liquids constitute a good example. In 2004, the group of Armstrong [76] published the first direct enantiomeric separation of compounds by using an ephedrinium-based stationary phase in gas chromatography. A *N,N*-dimethylephedrinium-based chiral ionic liquid, previously described by Wasserscheid, was coated on a fused-silica capillary column with a brown polyimide layer to generate a new chiral stationary phase, which was able to successfully separate a range of chiral alcohols and diols, chiral sulfoxides, and some chiral epoxides and acetamides.

Chiral ionic liquids may be associated in membranes through the development of SLMs, where an ionic liquid phase is immobilised inside the membrane porous support or through the development of membrane polymers integrating the chemistry of selected chiral ionic liquids (see previous discussion in this chapter). Making use of one of the most interesting advantages of membranes—contrarily to chromatographic processes, where particles are surrounded by a single environment, membranes can face two different environments simultaneously—integration with chiral ionic liquids can allow for a simultaneously enrichment of each contacting phase in a selected enantiomeric form. Alternatively, chiral ionic liquid-modified membranes can also be used in membrane chromatography processes.

4.5.3 Stimuli-Responsive Ionic Liquid Systems

Many ionic liquids contain transition metals. Therefore, it is not surprising that ionic liquids with pronounced magnetic properties have been described. Among the first examples were those reported by Okuno et al. [77], who

* Ephedrine = (R*,S*)-2-(methylamino)-1-phenylpropan-1-ol.

described the ionic liquid $[\text{C}_4\text{mim}][\text{FeCl}_4]$ as a material with a very large magnetic susceptibility and demonstrated that non-magnetic materials can be transported and separated readily in this ionic liquid with the help of magnetic-field gradients. Recently, ionic liquids responsive to magnetic-field gradients have been used in SLM systems showing adjustable transport properties for target solutes, based on the applied external magnetic field.

The facile tuneability of the physicochemical properties of ionic liquids can be used to modulate the wetting behaviour of polymer films and membranes. Recently [78], modified negatively charged polyimide films have been prepared using ionic liquids based on electrostatic self-assembly rather than using covalent links. To reveal the effect of anions on surface wettability, the authors screened a series of anions including Br^- , $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{NTf}_2]^-$, $[\text{OTf}]^-$, $[\text{ClO}_4]^-$, and $[\text{NO}_3]^-$. This was the first time that the reversible wettability of polymer surfaces was modulated using ionic liquids.

Like anions, the change in cations in ionic liquids also has the ability to modulate surface wettability, which was demonstrated by using the series $[\text{C}_2\text{mim}]\text{Br}$, $[\text{C}_4\text{mim}]\text{Br}$, $[\text{C}_6\text{mim}]\text{Br}$, and $[\text{C}_8\text{mim}]\text{Br}$ [78]. Using ionic liquids to modify surfaces provides a new strategy for reversible switching between hydrophobicity and hydrophilicity. However, the maximum contact angle can only reach up to 95° , and the highest change of contact angle is less than 45° . No switching between superhydrophobicity and superhydrophilicity via the exchange of counterions of ionic liquids has been reported yet.

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