

Understanding the Influence of the Ionic Liquid Composition and the Surrounding Phase Nature on the Stability of Supported Ionic Liquid Membranes

Francisco J. Hernández-Fernández, and Antonia P. de los Ríos

Dept. of Chemical and Environmental Engineering, Technical University of Cartagena, Campus La Muralla, C/ Doctor Fleming S/N, E-30202 Cartagena, Murcia, Spain

Francisca Tomás-Alonso

Dept. of Chemical Engineering, Faculty of Chemistry, University of Murcia, Campus de Espinardo, E-30100 Murcia, Spain

José M. Palacios

Dept. of Catalytic Process Engineering, Institute of Catalysis and Petrochemistry, Spanish Council for Scientific Research (CSIC), Campus de la UAM, Cantoblanco, 28049 Madrid, Spain

Gloria Villora

Dept. of Chemical Engineering, Faculty of Chemistry, University of Murcia, Campus de Espinardo, E-30100 Murcia, Spain

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The industrial application of supported liquid membranes (SLMs) is still limited due to concerns about their stability. In a previous work, the selective separation of the substrates and products of a transesterification reaction was successfully carried out using Nylon membranes impregnated with ionic liquids (ILs). This article analyses the effect of both the IL composition and the nature of the surrounding phase on the stability of these SLMs to design highly stable supported ionic liquid systems. For this purpose, the stability of SLMs based on several ILs after immersion for a week in different feed/receiving phases was characterized using scanning electron microscopy combined with energy dispersive X-ray (SEM-EDX). The differential migration of the ILs observed from the membrane toward the surrounding phases was found to be correlated with the solubility of the ILs in the contacting phases. It was observed that SLM stability increased as the polarity of the solvent used as receiving phase decreased and as the hydrophilic character of the ILs used as liquid phase increased. Furthermore, the polymeric support was found to have a strongly stabilizing effect because losses of IL after immersion in a given surrounding phase were much lower than that derived from the solubility of the IL in this phase. © 2011 American Institute of Chemical Engineers AICHE J, 58: 583–590, 2012

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Correspondence concerning this article should be addressed to F. J. Hernández-Fernández at antonia.perez@upct.es.

Introduction

Supported liquid membranes (SLMs) usually consist of an organic liquid embedded in the pores of a polymer support

retained by capillary forces. The use of such membranes for the selective separation of different chemical species is a promising technique as an attractive alternative to others conventional solvent extraction techniques. The most widely studied processes for selective separation are metal ions¹⁻³ and acids⁴⁻⁷ but neutral molecules, such as different drugs,^{8,9} phenols,^{10,11} and sugars¹²⁻¹⁴ have also been studied. This SLM system offers substantial advantages including low cost, high efficiency, and minimum product contamination. Furthermore, less extractant is required, there is no phase separation problem, no need for demulsification and scaling up for commercial applications is easy. However, despite all these advantages, the SLM technique is not fully utilized commercially at high scale, primarily due to its progressive performance decay with time. The instability of the organic liquid in the pores of the inert membrane as support reduces the period of utilization which has prevented its widespread use.¹⁵⁻²⁴

Various mechanisms have been proposed to explain the SLM instability: the loss of organic phase from the membrane through dissolution into the surrounding liquids, liquid migration due to pressure differences or osmotic pressure gradients,^{20,25} and emulsion formation²⁶ or attrition of the organic film^{21,26} due to lateral shear forces. Consequently, the SLM stability may also be affected by the chemical nature and textural properties of polymeric support, the type of organic solvent used in the studied process, the preparation method,^{27,28} etc., while the time periods for observed instability varies from a few hours to several months depending on the system.^{20,25} Many research groups have achieved SLMs with improved stability by a variety of means, including polymerization of the top layers,²⁹ gelation of a liquid membrane,^{22,30} and interposition of a highly permeable material.³¹ In addition to these studies, much attention has been paid to use of ionic liquids as liquid phase in SLMs.³²⁻³⁵

Ionic liquids (ILs), made of organic salts and liquids at room temperature, present numerous advantages over organic solvents conventionally used in separation processes as liquid phase in supported liquid membranes due to their negligible vapor pressure, the greater viscosity and the fact that their solubility in the surrounding phases can be controlled by adequate selection of the cation and anion.³⁶

The aim of this work was to get a better understanding of the influence of the ionic liquid composition and the nature of the surrounding phase on the stability of supported ionic liquid membranes to minimize the instability problems in SLMs previously used for the selective separation of transesterification reaction mixtures.³⁷ More specifically, SLMs based on [bmim⁺][NTf₂⁻], [bmim⁺][PF₆⁻], [bmim⁺][BF₄⁻], and [bmim⁺][Cl⁻] were prepared and characterized using scanning electron microscopy combined with energy dispersive X-ray (SEM-EDX). The assayed ILs have quite different hydrophilic characters and therefore allowed us to analyze the influence of this parameter on SLM stability. The SEM-EDX technique allowed us the characterization of the membrane surface morphologically, to examine the overall chemical composition of the membranes and ILs and their distribution. Fresh and after-operation SLMs in a cell 1 week's immersed in surrounding phases of different polarity including *n*-hexane/*n*-hexane, *n*-hexane/*tert*-butyl methyl ether (TBME), *n*-hexane/acetone, *n*-hexane/dimethyl sulfoxide (DMSO), and *n*-hexane/water. *n*-Hexane was used as

feeding phase in all cases, since it is the most commonly used organic solvent in transesterification reactions. These characterization studies allowed us not only to assess the presence of the ionic liquid in the membrane after preparation but also to identify whether there were any chemical modifications on the SILMs' surface after contact with the surrounding phases, thus providing valuable information about their integrity and stability.

Experimental

Reagents and membranes

A polymeric membrane of 25 mm diameter from Millipore S.A. (Madrid, Spain) was used as support with the following specifications: Nylon® HNWP -hydrophilic polyamide membrane- with a pore size of 0.45 μm and thickness of 170 μm.

The ionic liquids 1-butyl-3-methylimidazolium chloride, [bmim⁺][Cl⁻] (purity>99%), 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim⁺][BF₄⁻] (purity>99%) and 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim⁺][PF₆⁻] (purity>99%) were purchased from Solvent Innovation GmbH (Cologne, Germany). 1-Butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, [bmim⁺][NTf₂⁻] (purity >99%) was from Sigma-Aldrich-Fluka Chemical Co. (Madrid, Spain). Substrates, solvents and other chemicals were purchased from Sigma-Aldrich-Fluka Chemical Co. (Madrid, Spain), and were of the highest purity available.

Preparation of Supported Liquid Membranes. The preparation of supported liquid membranes was described in detail previously.³⁸ In brief, immobilization involved placing the membrane in a 10 mL AmiconTH ultrafiltration unit, to which 3 mL of ionic liquid was added before applying a nitrogen pressure of 2 bar. Pressure was released once a thin layer of ionic liquid was apparent on the upper surface of the membrane, indicating that all the pores were presumably full. Then, the membrane was left overnight in vertical position to remove by gravity all the excess ionic liquid located from the membrane surface.

Solubility of Ionic Liquids in Water and Organic Solvents. The solubility of the different ILs in water and organic solvents (*n*-hexane, TBME, acetone, and DMSO) was determined by using the "cloud point" method. For that, small aliquots of 5 μL of ionic liquid were successively added to the corresponding solvent and the mixture was vigorously stirred at 303.2 K for 5 min. The solubility of the ionic liquid in these solvents was determined by the appearance of turbidity in the sample.

Membrane Stability Studies. The stability studies were performed at 30°C using a glass diffusion cell with two independent compartments of 30 mL each one, separated by the respective SLM. *n*-hexane/*n*-hexane, *n*-hexane/TBME, *n*-hexane/acetone, *n*-hexane/DMSO, and *n*-hexane/water were used as feeding and receiving solutions, respectively. Both compartments were mechanically stirred continuously. The fresh and after-operation SLMs for 7 days in the diffusion cell were characterized by SEM-EDX immediately.

SEM-EDX Characterization. A scanning electron microscope (SEM) ISI DS-130 coupled to a Kevex Si/Li detector with an ultrathin window for the detection of chemical

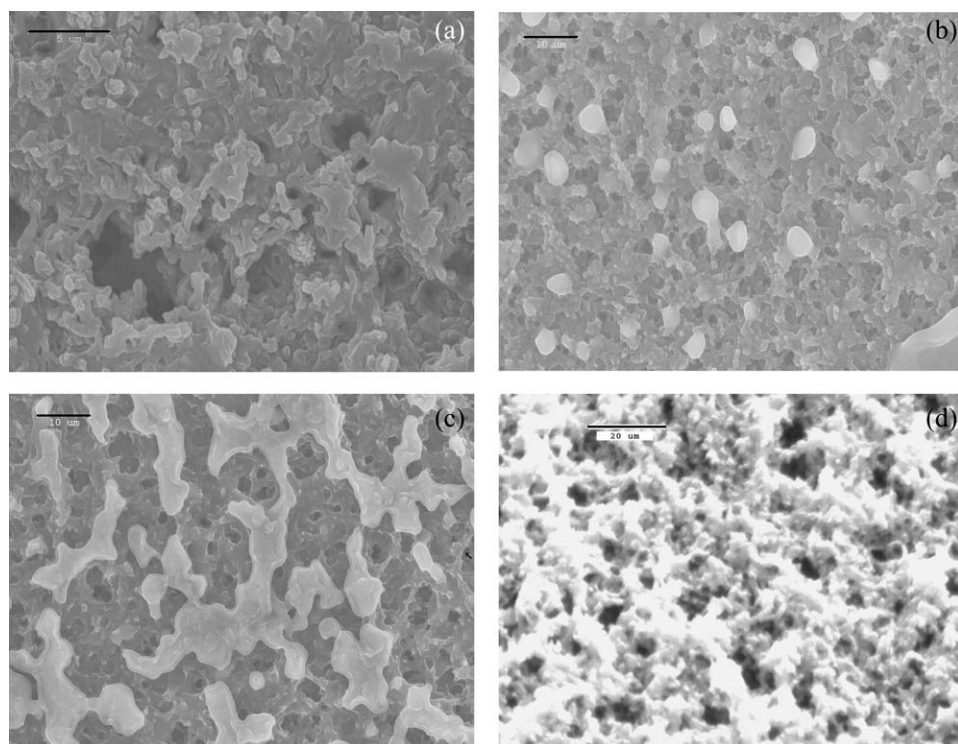


Figure 1. Scanning electron micrographs of the Nylon membrane impregnated with (a) $[\text{bmim}^+][\text{NTf}_2^-]$ (3040 \times) (scale bar = 5 μm), (b) $[\text{bmim}^+][\text{BF}_4^-]$ (1010 \times) (scale bar = 10 μm) (c) $[\text{bmim}^+][\text{PF}_6^-]$ (1010 \times) (scale bar = 10 μm), and (d) $[\text{bmim}^+][\text{Cl}^-]$ (1010 \times) (scale bar = 20 μm).

elements with $Z > 4$ (Be) and a Sun SparcStation 5 for energy dispersive X-ray (EDX) analysis was used to study the morphological appearance, the overall chemical composition, and the distribution of the chemical elements of interest in the supported liquid membranes.

Results and Discussion

Characterization of the supported liquid membranes

SEM micrographs of the Nylon membrane without IL (not shown) showed a highly porous material consisting of macropores of about 1 μm average size. The EDX spectrum of this Nylon membrane (not shown) showed the characteristic peaks assigned to the C $K\alpha$, O $K\alpha$, and N $K\alpha$ lines, the last two appearing as a single peak unresolved due to their proximity and small concentration. The presence of these chemical elements corresponds to the chemical formulation of polyamide. Hydrogen and other light elements that can be present in other samples can not be detected by EDX.

The supported ionic liquids studied: $[\text{bmim}^+][\text{NTf}_2^-]$, $[\text{bmim}^+][\text{PF}_6^-]$, $[\text{bmim}^+][\text{BF}_4^-]$ and $[\text{bmim}^+][\text{Cl}^-]$, respectively, were analyzed immediately after their immobilization in the membrane to assure the complete filling of the membrane pores verifying their homogeneous distribution. Figures 1a–d shows the SEM micrographs of the Nylon membrane impregnated with the four ILs.

The morphological study showed that, in general, after impregnation, the smaller pores of the membranes became occluded with ionic liquid and only the biggest ones remained

partially filled. These pictures also show that excess ionic liquid appeared on the external surface of the membranes: extensively in the case of $[\text{bmim}^+][\text{Cl}^-]$ (Figure 1d) and $[\text{bmim}^+][\text{PF}_6^-]$ (Figure 1c), moderately in the case of $[\text{bmim}^+][\text{BF}_4^-]$ (Figure 1b) and imperceptibly for $[\text{bmim}^+][\text{NTf}_2^-]$ (Figure 1a). As the preparation conditions were identical for all the ILs tested, these differential features seemed to be correlated with the viscosity of the respective ionic liquids, following the sequence: $[\text{bmim}^+][\text{Cl}^-] > [\text{bmim}^+][\text{PF}_6^-] > [\text{bmim}^+][\text{BF}_4^-] > [\text{bmim}^+][\text{NTf}_2^-]$.³⁹ Consequently, the accumulation of ionic liquid on the membrane surface seems to be a kinetic effect of liquid fluidity: the greater the IL viscosity, the higher the amount of IL remaining on the external surface of the membrane.

The EDX study of supported liquid membranes was carried out by selecting characteristic elements of interest in each ionic liquid: F and S for $[\text{bmim}^+][\text{NTf}_2^-]$, F and P for $[\text{bmim}^+][\text{PF}_6^-]$, F (B is not detected by EDX) for $[\text{bmim}^+][\text{BF}_4^-]$ and Cl for $[\text{bmim}^+][\text{Cl}^-]$, as shown in Figure 2. The relative peak heights of identical elements in the different membranes are approximately related with their respective concentrations assuming ZAF corrections are relatively negligible.

The presence of these characteristic peaks of the ionic liquids in the respective EDX spectrum of the fresh SLMs evidences that an amount of ionic liquid remains adsorbed in their respective Nylon membrane.

Membrane Stability Studies. Stability experiments were carried out to investigate the possible loss of ionic liquid from the Nylon membrane pores during operation when

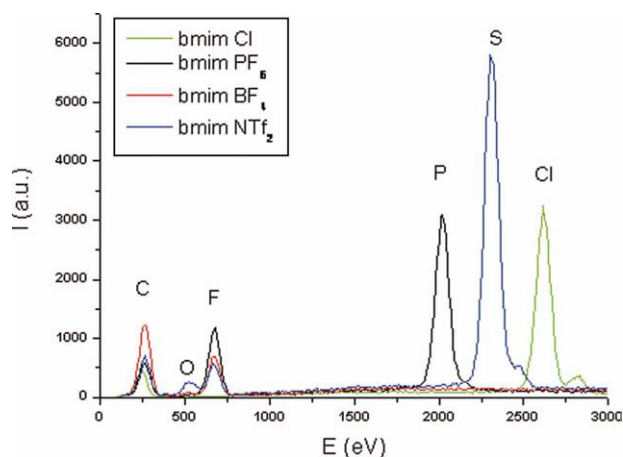


Figure 2. EDX spectra of the Nylon membrane impregnated with [bmim⁺][NTf₂⁻], [bmim⁺][PF₆⁻], [bmim⁺][BF₄⁻], and [bmim⁺][Cl⁻].

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surrounding phases of different Snyder polarity index were used. This polarity scale is an overall measure of solvent strength and is a composite of three types of solvent-solute interactions: dipole-type, hydrogen-bond base, and hydrogen bond acid.⁴⁰ *n*-Hexane/*n*-hexane (Polarity index_{*n*-hexane} = 0.1), *n*-hexane/TBME (Polarity index_{TBME} = 2.4), *n*-hexane/acetone (Polarity index_{acetone} = 5.1), *n*-hexane/DMSO (Polarity index_{DMSO} = 7.2), and *n*-hexane/water (Polarity index_{water} = 10.2) were used as feed and receiving solutions, respectively. *n*-Hexane was used as feed phase in all cases since our future interest is to use these SLMs in reaction/separation processes for the kinetic resolution of racemic alcohols by enzymatic transesterification reactions and *n*-hexane is one of the most commonly used organic solvent in these processes. Solvents used as receiving phases were chosen with the aim of covering the full range of polarity index (0 to 10.2). These experiments were performed by keeping the membranes with a supported IL ([bmim⁺][NTf₂⁻], [bmim⁺][PF₆⁻], [bmim⁺][BF₄⁻], or [bmim⁺][Cl⁻]) immersed for a week in a diffusion cell with two independent compartments. The membranes were then characterized by SEM-EDX analysis to examine the overall chemical composition of the membranes, characterize the membrane surface morphologically and examine the distribution of the ILs within them.

The morphological aspect of the Nylon membrane impregnated with [bmim⁺][NTf₂⁻] after cell operation in hexane/hexane (not shown) was identical to that of the fresh supported liquid membrane based on [bmim⁺][NTf₂⁻] shown in Figure 1a. Furthermore, the SEM-EDX spectra taken from this membrane before and after immersion in the *n*-hexane/*n*-hexane (Figure 3) were very similar, indicating that the amount of ionic liquid retained in the after-operation membrane is similar. Consequently, the membrane is stable against the possible solvent action of *n*-hexane. The SEM-EDX spectrum of the SLM after immersion in the hexane/TBME (see Figure 3) indicated that part of the ionic liquid retained in the membrane pores had disappeared during cell operation. The SLM membrane is only partially stable under

TBME. When *n*-hexane/acetone, *n*-hexane/DMSO, and *n*-hexane/water were used as feeding/receiving phases, the respective SEM-EDX spectra of the after-test membranes showed the almost complete absence of the F and S peaks characteristic of this IL indicating that the IL is dissolved in the surrounding liquid and that the SLM is not stable in these solvents (see Figure 3).

Similarly, the morphology of the Nylon membrane impregnated with IL [bmim⁺][PF₆⁻] after-operation in the diffusion cell (surrounding phase: *n*-hexane/*n*-hexane) determined by SEM (not shown), showed that most of the ionic liquid located on the external membrane surface was swept off during cell operation. Comparison of the SEM-EDX spectra taken from membranes before and after immersion in the hexane/hexane solution (Figure 4) was very similar. Since the EDX spectra are taken from a sample depth of up to a few micrometers and, consequently, show the contribution of ionic liquid occluded within the membrane pores, it can be concluded that the amount of ionic liquid retained in the membrane pores is apparently kept constant after operation and the SLM membrane is stable under *n*-hexane. As can be also seen from Figure 4, this SLM showed a similar behavior in hexane/TBME. Finally, a complete absence of IL in the SLM after immersion in hexane/acetone, *n*-hexane/DMSO, and *n*-hexane/water was observed by SEM micrographs (not shown), which was also confirmed by their respective SEM-EDX spectra, since the F and P peaks characteristic of this IL were not detected (see Figure 4). The studied SLM is not stable under acetone, DMSO, and water.

The SEM micrographs of the Nylon membrane impregnated with [bmim⁺][BF₄⁻] after cell operation in *n*-hexane/*n*-hexane and *n*-hexane/TBME (not shown) showed that the IL were still retained within the membrane pores. Furthermore, we observed that some brilliant spots, due to ionic liquid drops located on the external surface of the membrane, are still remaining after operation indicating is high stability.

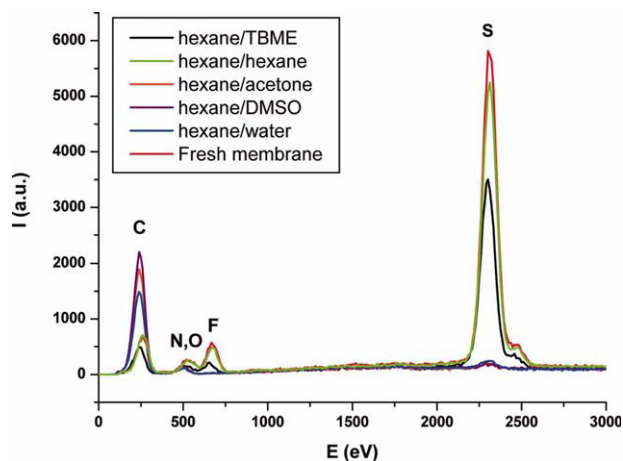


Figure 3. EDX spectra of the Nylon membrane impregnated with [bmim⁺][NTf₂⁻] before and after immersion in *n*-hexane/*n*-hexane, *n*-hexane/TBME, *n*-hexane/acetone, *n*-hexane/DMSO, and *n*-hexane/water.

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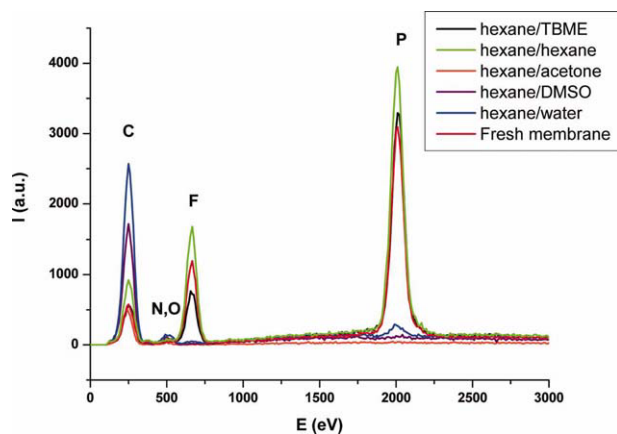


Figure 4. EDX spectra of the Nylon membrane impregnated with $[\text{bmim}^+][\text{PF}_6^-]$ before and after immersion in *n*-hexane/*n*-hexane, *n*-hexane/TBME, *n*-hexane/acetone, *n*-hexane/DMSO, and *n*-hexane/water.

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Additionally, the SEM-EDX spectra taken from the membrane before and after immersion in the *n*-hexane/*n*-hexane and *n*-hexane/TBME solutions (see Figure 5) were very similar, and the similar intensity of the characteristic peaks indicates that the amount of ionic liquid retained in the membrane is constant. Consequently, the membrane is stable in the presence of *n*-hexane and TBME. However, when acetone, DMSO or water were used as receiving phases the morphological appearance of the after-operation SLMs were identical to that of the fresh Nylon membranes, indicating the complete absence of ionic liquid (data not shown). The SEM-EDX spectra of the after-operation membranes confirmed this feature since they pointed to the complete absence of the F peak characteristic of this IL (Figure 5).

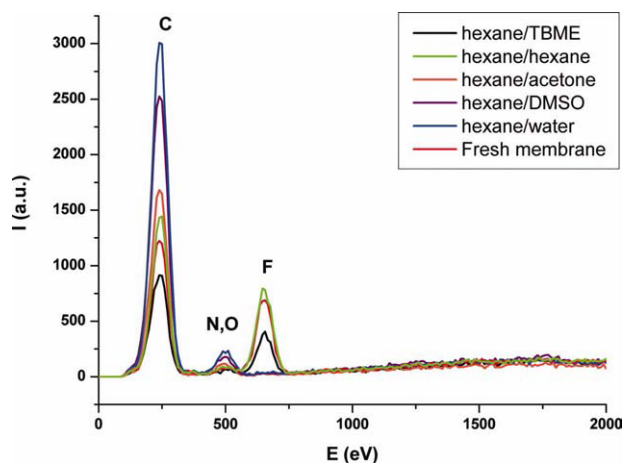


Figure 5. EDX spectra of the Nylon membrane impregnated with $[\text{bmim}^+][\text{BF}_4^-]$ before and after immersion in *n*-hexane/*n*-hexane, *n*-hexane/TBME, *n*-hexane/acetone, *n*-hexane/DMSO, and *n*-hexane/water.

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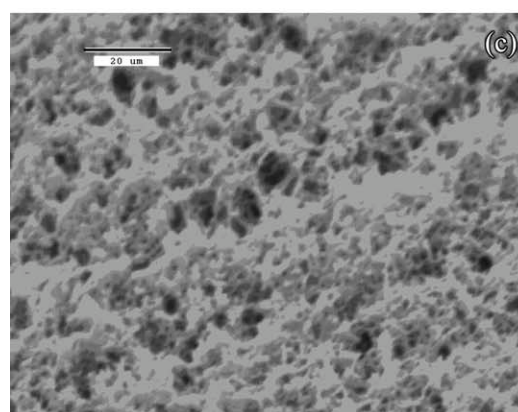
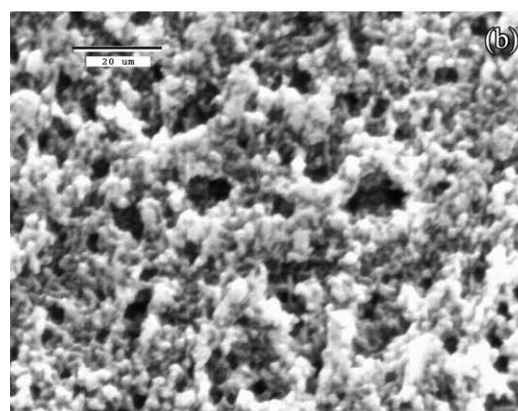
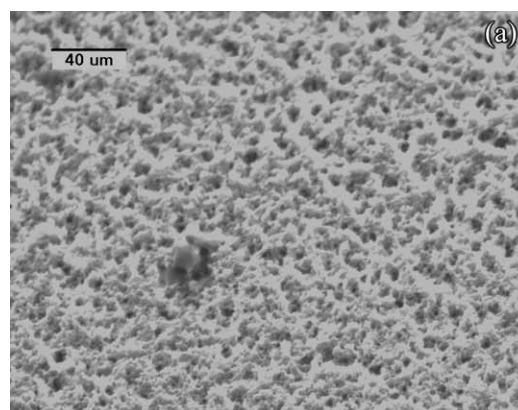


Figure 6. Scanning electron micrographs of the Nylon membrane impregnated with $[\text{bmim}^+][\text{Cl}^-]$ after immersion in (a) *n*-hexane/*n*-hexane (1010 \times) (scale bar = 40 μm), (b) *n*-hexane/TBME (1010 \times) (scale bar = 20 μm), (c) *n*-hexane/acetone (1010 \times) (scale bar = 20 μm).

Similarly, the morphological aspect of the Nylon membrane impregnated with $[\text{bmim}^+][\text{Cl}^-]$ after cell operation in hexane/hexane (Figure 6a), hexane/TBME (Figure 6b) and hexane/acetone (Figure 6c) is similar to that of the fresh supported liquid membrane depicted in Figure 1d. Even the IL located on the external surface of the membrane was not swept off after operation. The SEM-EDX spectra taken from the membrane before and after immersion in these solvents (Figure 7) were very similar, confirming that the SLM based

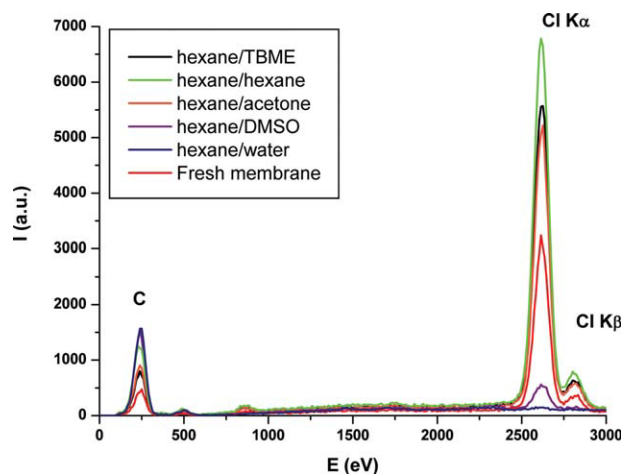


Figure 7. EDX spectra of the Nylon membrane impregnated with [bmim⁺][Cl⁻] before and after immersion in *n*-hexane/*n*-hexane, *n*-hexane/TBME, *n*-hexane/acetone, *n*-hexane/DMSO, and *n*-hexane/water.

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on [bmim⁺][Cl⁻] was stable with *n*-hexane, TBME, and acetone. The absence of IL in the SLM after immersion *n*-hexane/DMSO and *n*-hexane/water was evident from the SEM micrographs (not shown), which was also confirmed by their respective SEM-EDX spectra, the Cl peak characteristic of this IL not being detected (see Figure 7). This SLM is not stable in the presence of DMSO or water.

The quantitative results obtained by weight differences of the SLMs before and after 7 days operation in the diffusion cell corroborate the results obtained by SEM-EDX, as shown in Table 1.

The observed differential migration of the ionic liquids from the Nylon membrane to the surrounding phases might be explained by taking into account the different degrees of solubility of the ionic liquids in the contacting phases. Table 2 shows the solubility of the assayed ionic liquids in the solvents used as receiving phase. As can be observed in this table, the stability of the SLM based on [bmim⁺][BF₄⁻] is correlated with the solubility of this IL in the organic solvents used as surrounding phases. In addition, the limited solubility of the ionic liquid [bmim⁺][Cl⁻] in acetone could explain the stability of the SLM based on [bmim⁺][Cl⁻] in this solvent. It should be mentioned that in this case, the losses of IL were lower than might be expected from the solubility study (immobilized IL: 89 mg, losses of IL: 40 mg, maximum IL solubilized in acetone: 157 mg), which underlines the stabilizing effect of the polymeric support in the SLM. This fact could be explained by its higher viscosity,^{39,41} which could reduce the displacement of this ionic liquid from the micron pores of the SLM. Furthermore, the increase in the hydrophilic character of the ILs ([bmim⁺][NTf₂⁻] < [bmim⁺][PF₆⁻] < [bmim⁺][Cl⁻] < [bmim⁺][BF₄⁻])⁴² also resulted in a reduction of its solubility in the surrounding phases (with the exception of water), therefore, increasing the stability of the resulting SLM. When a highly polar liquid is used as the receiving phase (water) the sequence of

Table 1. Ionic Liquid Losses in the SLMs after 7 days' Operation in Different Surrounding Phases Determined by Mass Balance Method

SLM	Feed/Receiving Phases	IL Losses (%)
Hexane/Hexane	Nylon with [bmim ⁺][Cl ⁻]	0.4
	Nylon with [bmim ⁺][BF ₄ ⁻]	0.5
	Nylon with [bmim ⁺][PF ₆ ⁻]	0.7
	Nylon with [bmim ⁺][NTf ₂ ⁻]	0.1
Hexane/TBME	Nylon with [bmim ⁺][Cl ⁻]	12.4
	Nylon with [bmim ⁺][BF ₄ ⁻]	12.6
	Nylon with [bmim ⁺][PF ₆ ⁻]	15.7
	Nylon with [bmim ⁺][NTf ₂ ⁻]	49.8
Hexane/Acetone	Nylon with [bmim ⁺][Cl ⁻]	45.0
	Nylon with [bmim ⁺][BF ₄ ⁻]	64.7
	Nylon with [bmim ⁺][PF ₆ ⁻]	99.3
	Nylon with [bmim ⁺][NTf ₂ ⁻]	99.8
Hexane/DMSO	Nylon with [bmim ⁺][Cl ⁻]	99.3
	Nylon with [bmim ⁺][BF ₄ ⁻]	99.7
	Nylon with [bmim ⁺][PF ₆ ⁻]	99.4
	Nylon with [bmim ⁺][NTf ₂ ⁻]	99.8
Hexane/Water	Nylon with [bmim ⁺][Cl ⁻]	100.0
	Nylon with [bmim ⁺][BF ₄ ⁻]	99.6
	Nylon with [bmim ⁺][PF ₆ ⁻]	99.2
	Nylon with [bmim ⁺][NTf ₂ ⁻]	98.5

solubility is the contrary. These observations highlight the important role played by the hydrophilic/hydrophobic character of the ionic liquid on the design of SILMs.

The stability can also be correlated with the polarity of the surrounding phases (see Table 1). IL losses decreased with decreasing polarity of the solvent used as receiving phase (water > DMSO > acetone > TBME > *n*-hexane). Having in mind the polarity index sequence of the solvent used as receiving phase, it can be concluded that ionic liquid losses were not significant when the polarity index of the solvent used as receiving phase was lower than 2.5. These results allow us to choose the most suitable organic solvents for use as surrounding phases.

The homogeneity of the samples was studied by SEM-EDX line profiles of the characteristic elements of the four supported liquid membranes. Figure 8 shows the respective

Table 2. Solubility of the Assayed Ionic Liquids in the Solvents used as Receiving Phase

Ionic Liquid	Solvent	Solubility (% v/v)
[bmim ⁺][NTf ₂ ⁻]	<i>n</i> -hexane	< 0.005
	TBME	< 0.217
	Acetone	Miscible
	DMSO	Miscible
	Water	< 0.280
[bmim ⁺][PF ₆ ⁻]	<i>n</i> -hexane	< 0.005
	TBME	< 0.005
	Acetone	Miscible
	DMSO	Miscible
	Water	< 0.501
[bmim ⁺][BF ₄ ⁻]	<i>n</i> -hexane	< 0.005
	TBME	< 0.005
	Acetone	Miscible
	DMSO	Miscible
	Water	Miscible
[bmim ⁺][Cl ⁻]	<i>n</i> -hexane	< 0.005
	TBME	< 0.005
	Acetone	< 0.483
	DMSO	Miscible
	Water	Miscible

line profiles of the four SLMs after operation in hexane/TBME. The profiles indicate that the distribution of the IL was quite homogeneous with small inhomogeneities due to the macroporous nature of the Nylon membrane.

The evolution of the progressive loss ionic liquid in SLM can be understood by comparing the respective EDX line profiles of an ionic liquid in the different surrounding phases of different polarity. As an example, the line profiles of after-operation SLMs based on $[\text{bmim}^+][\text{Cl}^-]$ are shown in Figure 9. As commented above, the losses of ionic liquid increased in the order: *n*-hexane < TBME < acetone and the line profiles reveal that the homogeneity increases in this same order. The SLM homogeneity is mostly given by the filling of membrane pores by the ionic liquid. EDX line profiles indicate that the sample homogeneity increases as the ionic losses increase from *n*-hexane to acetone. This homogeneity evolution suggests that the ionic liquid loss starts in that retained in the macropores, then extending to that contained in the mesopores.

Conclusions

Scanning electron-microscopy (SEM) combined with Energy Dispersive X-ray (EDX) analysis was used to microscopically characterize the stability of supported membranes based on ionic liquids after immersion in different surrounding phases. The differential migration of the ionic liquids from the polymeric membrane toward the surrounding phases can be attributed to the different degrees of solubility of the ionic liquids in the contacting phases. In this context, a proper design of an IL including cation and anion composition could reduce its solubility in the surrounding phases, therefore, increasing the stability of the SLM.

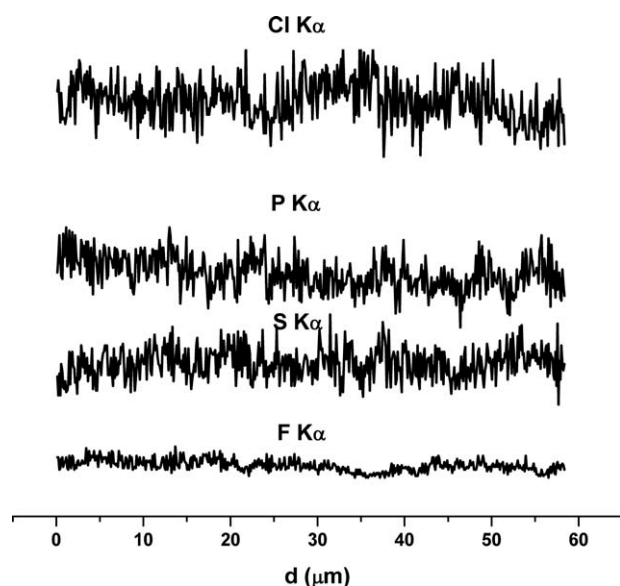


Figure 8. SEM-EDX line profiles of the $K\alpha$ line of the characteristic element of the four supported liquid membranes based on $[\text{bmim}^+][\text{NTf}_2^-]$, $[\text{bmim}^+][\text{PF}_6^-]$, $[\text{bmim}^+][\text{BF}_4^-]$, and $[\text{bmim}^+][\text{Cl}^-]$ after 7 days operation in hexane/TBME.

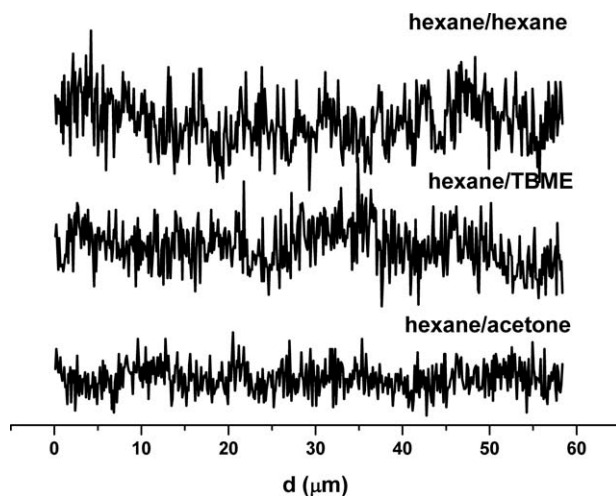


Figure 9. SEM-EDX line profiles of $\text{Cl } K\alpha$ in Nylon membranes impregnated with $[\text{bmim}^+][\text{Cl}^-]$ after 7 days operation in hexane/hexane, hexane/TBME, and hexane/acetone.

Two parameters were found to constitute a useful tool for designing highly stable supported ionic liquid membranes with no need for prior experimentation: the hydrophilicity of the ionic liquid used as liquid phase in the SLM and the polarity of the surrounding phases. Furthermore, an important stabilizing effect of the polymeric membrane was observed since the losses of IL determined by weight difference were lower than that attributed to the solubility of the ILs in the surrounding phases.

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Literature Cited

- Bansal B, Chen XD, Hossain MDM. Transport of lithium through a supported liquid membrane of LIX54 and TOPO in kerosene. *Chem Eng Process.* 2005;44:1327–1336.
- Alguacil FJ, Navarro P. Permeation of cadmium through a supported liquid membrane impregnated with Cyanex 923. *Hydrometallurgy.* 2001;61:137–142.
- de los Ríos AP, Hernández-Fernández FJ, Lozano LJ, Sánchez S, Moreno JI, Godínez C. Removal of Metal ions from aqueous solutions by extraction with ionic liquids. *J Chem Eng Data.* 2010, 55: 605–608.
- Schlosser S, Kertész R, Marták J. Recovery and separation of organic acids by membrane-based solvent extraction and pertraction: an overview with a case study on recovery of MPCA. *Sep Purif Technol.* 2005;41:237–266.
- Juang R-S, Chen L-J. Transport of citric acid across a supported liquid membrane containing various salts of a tertiary amine. *J Membr Sci.* 1997;123:81–87.
- Juang R-S, Huang R-H. Kinetic studies on lactic acid extraction with amine using a microporous membrane-based stirred cell. *J Membr Sci.* 1997;129:185–196.
- Juang R-S, Lee S-H, Shiau R-C. Mass-transfer modeling of permeation of lactic acid across amine-mediated supported liquid membranes. *J Membr Sci.* 1997;137:231–239.

8. Rios C, Salvadó V, Hidalgo M. Facilitated transport and preconcentration of the herbicide glyphosate and its metabolite AMPA through a solid supported liquid-membrane. *J Membr Sci.* 2002;203:201–208.
9. Ishizu H, Habaki H, Kawasaki J. Permeation and concentration of compactin by a liquid membrane technique. *J Membr Sci.* 2003;213:209–219.
10. Park S-W, Kim K-W, Sohn I-J, Kaseger C-F. Facilitated transport of sodium phenolate through supported liquid membrane. *Sep Purif Technol.* 2000;19:43–54.
11. Le QTH, Ehler DS, McCleskey TM, Dye RC, Pesiri DR, Jarvinen GD, Sauer NN. Ultra-thin gates for the transport of phenol from supported liquid membranes to permanent surface modified membranes. *J Membr Sci.* 2002;205:213–222.
12. Bartsch RA, Way JD, editors. *Chemical Separations with Liquid Membranes*, A.C.S. Symposium Series, vol. 642. Washington, DC: ACS, 1996 (Chapter 1).
13. Noble RD, Way JD, editors. *Liquid Membranes: Theory and Applications*, A.C.S. Symposium Series, vol. 347. Washington, DC: ACS, 1987:111–121.
14. Sastre AM, Kumar A, Shukla JP, Singh RK. Improved techniques in liquid membrane separations: an overview. *Sep Purif Methods.* 1998;27:213–298.
15. Danesi PR, Reichley-Yinger L, Rickert PG. Lifetime of supported liquid membranes: the influence of interfacial properties, chemical composition and water transport on the long-term stability of the membranes. *J Membr Sci.* 1987;31:117–145.
16. Takeuchi H, Takahashi K, Goto W. Some observations on the stability of supported liquid membranes. *J Membr Sci.* 1987;34:19–31.
17. Neplenbroek AM, Bargeman D, Smolders CA. The stability of supported liquid membranes. *Desalination.* 1990;79:303–312.
18. Chiarizia R. Stability of supported liquid membranes containing long-chain aliphatic amines as carriers. *J Membr Sci.* 1991;55:65–77.
19. Neplenbroek AM, Bargeman D, Smolders C. Nitrate removal using supported liquid membranes: transport mechanism. *J Membr Sci.* 1992;67:107–119.
20. Neplenbroek AM, Bargeman D, Smolders CA. Supported liquid membranes: instability effects. *J Membr Sci.* 1992;67:121–132.
21. Neplenbroek AM, Bargeman D, Smolders CA. Mechanism of supported liquid membrane degradation: emulsion formation. *J Membr Sci.* 1992;67:133–148.
22. Neplenbroek AM, Bargeman D, Smolders CA. Supported liquid membranes: stabilization by gelation. *J Membr Sci.* 1992;67:149–165.
23. Hill C, Dozol J-F, Rouquette H, Eymard S, Tournois B. Study of the stability of some supported liquid membranes. *J Membr Sci.* 1996;114:73–80.
24. He T, Versteeg LAM, Mulder MHV, Wessling M. Composite hollow fiber membranes for organic solvent-based liquid-liquid extraction. *J Membr Sci.* 2004;234:1–10.
25. Kemperman AJB, Bargeman D, vandenBoomgaard T, Strathmann H. Stability of supported liquid membranes: state of the art. *Sep Sci Technol.* 1996;31:2733–2762.
26. Dreher TM, Stevens GW. Instability mechanisms of supported liquid membranes. *Sep Sci Technol.* 1998;33:835–853.
27. Zhang B, Gozzelino G, Baldi G. Membrane liquid loss of supported liquid membrane based on n-decanol. *Colloid Surface A.* 2001;193:61–70.
28. Yang XJ, Fane T. Effect of membrane preparation on the lifetime of supported liquid membranes. *J Membr Sci.* 1997;133:269–273.
29. Kemperman AJB, Rolevink HHM, Bargeman D, van den Boomgaard T, Strathmann H. Stabilization of supported liquid membranes by interfacial polymerization top layers. *J Membr Sci.* 1998;138:43–55.
30. Kemperman AJB, Damink B, van den Boomgaard T, Strathmann H. Stabilization of supported liquid membranes by gelation with PVC. *J Appl Polym Sci.* 1997;65:1205–1216.
31. Wijers MC, Jin M, Wessling M, Strathmann H. Supported liquid membranes modification with sulphonated poly(ether ether ketone) permeability, selectivity and satiability. *J Membr Sci.* 1998;147:117–130.
32. Scovazzo P, Visser AE, Davis JH, Rogers RD, Koval CA, Dubois DL, Noble RD. *Supported Ionic Liquid Membranes and Facilitated Ionic Liquid Membranes.* ACS Symp. Ser. 818 (Ionic Liquid), 2002:69–87 (Chapter 6). ACS Publications, Washington.
33. Fortunato R, Afonso CAM, Benavente J, Rodriguez-Catellon E, Crespo JG. Stability of supported ionic liquid membranes as studies by X-ray photoelectron spectroscopy. *J Membr Sci.* 2005;256:216–223.
34. Schmidt C, Glück T. Schmidt–Naake Modification of Nafion membranes by impregnation with ionic liquids. *Chem Eng Technol.* 2008;31:13–22.
35. Marták J, Schlosser S, Vlcková S. Pertraction of lactic acid through supported liquid membranes containing phosphonium ionic liquid. *J Membr Sci.* 2008;318:298–310.
36. Teramoto M, Sakaida Y, Fu SS, Ohnishi N, Matsuyama H, Fukui T, Arai K. Attempt for the stabilization of supported liquid membrane. *Sep Purif Technol.* 2000;21:137–142.
37. de los Ríos AP, Hernández-Fernández FJ, Tomás-Alonso F, Rubio M, Gómez D, Villora G. On the importance of the nature of the ionic liquids in the selective simultaneous separation of the substrates and products of a transesterification reaction through supported ionic liquid membranes. *J Membr Sci.* 2008;307:233–238.
38. Hernández-Fernández FJ, de los Ríos AP, Rubio M, Tomás-Alonso F, Gómez D, Villora G. A novel application of supported liquid membranes based on ionic liquids to the selective simultaneous separation of the substrates and products of a transesterification reaction. *J Membr Sci.* 2007;293:73–80.
39. Li D, Zhang Y, Wang H, Tang J, Wang B. Effect of the medium on the stereostructure of poly(methyl methacrylate) synthesized in ionic liquids. *J Appl Polym Sci.* 2006;102:2199–2202.
40. Snyder LR. Classification of the solvent properties of common liquids. *J Chromatogr Sci.* 1978;16:223–234.
41. Tukuda H, Tsuzuki S, Susan ABH, Hayamizu K, Watanabe M. How ionic are room-temperature ionic liquids? An indicator of the physicochemical properties. *J Phys Chem B.* 2006;110:19593–19600.
42. Ropel L, Belvèze LS, Aki SNVK, Stadtherr AM, Brennecke JF. Octanol-water partition coefficients of imidazolium-based ionic liquids. *Green Chem.* 2005;7:83–90.

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