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Review

Recent advances in supported ionic liquid membrane technology

L.J. Lozano[a,*], C. Godínez[a], A.P. de los Ríos[a], F.J. Hernández-Fernández[a],
S. Sánchez-Segado[a], F.J. Alguacil[b]

[a] Department of Chemical and Environmental Engineering, Technical University of Cartagena, Campus La Muralla, C/Doctor Fleming S/N, E-30202 Cartagena, Murcia, Spain
[b] National Center for Metallurgical Research, Spanish National Research Council (CENIM-CSIC), Avda. Gregorio del Amo, 8, Ciudad Universitaria, E-28040 Madrid, Spain

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ABSTRACT

Novel processes based on supported liquid membranes have been proposed as effective methods for the selective separation of different chemical species in dilute streams, such as metal ions, organic compounds or biologically important compounds and gas mixtures. However, the industrial use of supported liquid membranes based on conventional liquids is limited by their relative instability and short lifetime. The use of ionic liquids as a liquid membrane phase could overcome these inconveniences due to their negligible vapour pressure and the possibility of minimizing their solubility in the surrounding phases by adequate selection of the cation and anion. The possibility of designing suitable ionic liquids for specific separation problems has also opened up new potential fields of industrial application of supported ionic liquid membranes. In this review an overview is given of recent advances in supported membranes based on ionic liquids, including issues such as methods of preparation, transport mechanisms, configurations, stability, fields of application and process intensification using supported ionic liquid membranes.

Contents

1. Introduction

Membrane science has taken its place among the most important topics of research in the world today, with sales of membrane systems topping US$ 1 billion annually [1]. Among the processes being developed, supported liquid membranes (SLMs), porous supports whose pores are impregnated with a solvent, have been

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[*] Corresponding author. Tel.: +34 968 325 416.
E-mail address: luisja.lozano@upct.es (L.J. Lozano).

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showing tremendous potential in different applications [2–4]. The SLM technique is a combination of three simultaneously occurring processes: molecule extraction from the feed phase to the SLM, diffusion through SLM and re-extraction to the received phase. Among their numerous advantages are specificity, the minimal amount of solvent needed and the fact that extraction and stripping steps are combined into a single step [5]. Unfortunately, few large scale SLM applications are found in the literature, mainly due to insufficient membrane stability [6,7]. To explain this low SLM stability various mechanisms have been proposed: loss of organic phase from the supporting membrane, either by evaporation or dissolution/dispersion into the adjacent phases, pressure difference, etc. [8]. Unlike the solvents previously used in SLMs, ILs possess unique properties that are interesting in the context of liquid membranes [9–11].

ILs are organic salts remaining as liquids under ambient temperatures. They normally consist of an organic cation (e.g. imidazolium, pyridinium, pyrrolidinium, phosphonium, ammonium), and a polyatomic inorganic anion (e.g. tetrafluoroborate, hexafluorophosphate, chloride) or, more and more current, an organic anion (e.g. trifluoromethylsulfonate, bis[(trifluoromethyl)sulfonyl]imide) [12]. The structures of common cations and anions of ILs are shown in Fig. 1. The main advantage of these media are their near-zero vapour pressure and their good chemical and thermal stabilities, having a large temperature range where they are stable with a negligible vapour pressure. Therefore, they have been considered as environmental benign solvents as compared to volatile organic solvents. Additionally, the properties of ionic liquids (hydrophobicity, viscosity, solubility, etc.) can be varied by altering the substitutive group on the cation or the combined anion [12,13] to make them more widely applicable in many physical and chemical fields. Indeed, ionic liquids have been used in replacement of volatile organic solvents in a wide variety of chemical processes at laboratory scale, such as separation and purification [14–20], reaction media in biochemical [21–23] and chemical catalysis [24–27].

The use of these new solvents as a liquid membrane phase results in the stabilization of the SLMs due to their negligible vapour pressure, the possibility of minimizing their solubility in the surrounding phases by adequate selection of the cation and anion [28], and their high viscosity (up to 500 cP) which could slow down the displacement of the liquids from the micron pores under pressure. Other interesting properties of ILs in the context of liquid membranes are their high ion conductivity [29] and high solvent power [30]. All these mentioned properties have led ILs to being considered “green designer solvents” [31].

In the last decade some researchers have reported that SLMs based on ILs achieved selective transport organic compounds such as amines, alcohols, organic acids, ketones, ethers, and aromatic hydrocarbons [14,15,17,32,33], mixed gases [34,35] and metal ions [36–38]. This review focuses on the development and application of supported ionic liquid membranes. An overview of the recent advances in supported ionic liquid membrane technology is given, including issues such as methods of preparation, transport mechanisms, configurations, stability, fields of application and process intensification using supported ionic liquid membranes.

2. Methods of preparation of supported ionic liquid membranes

Due to the relatively high viscosity of the ionic liquids, the method of preparation of supported ionic liquid membranes can play an important role on the membrane performance. Three methods are commonly used for the preparation of supported ionic liquid membranes: direct immersion, pressure or vacuum [18,39,40]. In the former case, immobilization takes places by contacting the supporting membrane with the ionic liquid, allowing it to soap up the liquid [18]. In the pressure method, the immobilization is achieved by placing the membrane in an ultrafiltration unit, adding an amount of ionic liquid and applying nitrogen pressure to force the ionic liquid to flow into the pores of the membrane, and therefore, displacing air from the pores of the membrane with the ionic liquid [39]. In the vacuum method, the supporting membrane is submerged in a volume of IL and vacuum is applied to release all air occluded in the pores of the membranes [40]. After all procedures, the excess ionic liquid should be removed from the membrane surface either by leaving to drip overnight or by blotting with paper tissue.

Scanning electron microscopy (SEM) combined with energy dispersive X-ray (EDX) analysis was used to analyse the influence of the immobilization method on the SILMs performance [39]. This technique allows the characterization of the membrane surface morphology and the examination the global chemical composition of the membranes and the distribution of the ILs within them. Fig. 2 shows examples of SEM micrographs of a plain Nylon membrane and supported liquid membranes based on $[\text{bmim}^+][\text{PF}_6{}^-]$ prepared by using the pressure and the vacuum methods, respectively.

The morphological study showed that, after impregnation by either method, the IL was homogeneously distributed in the pores of the membrane, except for the largest macropores that remained partially filled. These pictures also show the presence of a small amount of excess IL located on the external membrane surface. The SEM–EDX and weight studies showed that the amount of IL immobilized was independent of the ionic liquid used when the immobilization was carried out under pressure. In contrast, following immobilization under vacuum, less ionic liquid was adsorbed into the membranes when more viscous ILs were used. This behaviour could be explained by the fact that the high viscosity of these ILs makes it difficult their penetration into the middle of the deeper pores of the membrane under vacuum. From these findings it was concluded that immobilization under vacuum can be considered suitable for low viscosity ionic liquids, with the added advantage that it is also an easier preparation method. However, for high viscosity ionic liquids, immobilization of the ionic liquid should use pressure in order to ensure that all membrane pores are filled with liquid.

The nature of the supporting membrane also plays an important role in the performance of supporting ionic liquid membranes. In this context, De los Rios et al. [9] studied the used of two polymeric membranes, Nylon and Mitex, as supporting membranes. Nylon membrane was a hydrophilic polyamide membrane with a pore size of 0.45 μm and a thickness of 170 μm. Mitex membrane was a hydrophobic polytetrafluoroethylene membrane with a pore size of 10 μm and a thickness of 130 μm. It was observed that less ionic liquid was absorbed into the Mitex membranes, which was explained by the different textural properties and the high hydrophobic character of these membranes, which probably restrict interaction with the hydrophilic ionic liquids [41] used. Simple determination of the wettability has been also used as criteria in the selection of a proper supporting membrane [32].

The use of nanofiltration membranes as supporting membranes has been also reported [42]. In this case, direct filtration of ionic liquids through the nanofiltration membrane was not possible at a gas pressure up to 7 bar. The ionic liquids make up of cations which contain straight or branched hydrocarbon chains were easily absorbed into the polymeric membrane allowing the nanoporous structure soaked up and saturated with the ionic liquids.