Studies on the Selective Transport of Organic Compounds by Using Ionic Liquids as Novel Supported Liquid Membranes

Luís C. Branco, João G. Crespo, and Carlos A. M. Afonso*[a]

Abstract: The possibility of using room-temperature ionic liquids (RTILs) in bulk (nonsupported) and supported liquid membranes for the selective transport of organic molecules is demonstrated. A systematic selective transport study, in which 1,4-dioxane, propan-1-ol, butan-1-ol, cyclohexanol, cyclohexanone, morpholine, and methylmorpholine serve as a model seven-component mixture of representative organic compounds, and in which four RTILs based on the 1-*n*-alkyl-3-methylimidazolium cation (*n*-butyl, *n*-octyl, and *n*-decyl) are used together with the anions PF_6^- or BF_4^-, immobilized in five different supporting membranes, confirms that the combination of the selected RTILs with the supporting membranes is crucial to achieve good selectivity for a specific solute. The use of the RTIL 1-*n*-butyl-3-methylimidazolium hexafluorophosphate, immobilized in a polyvinylidene fluoride membrane, allows an extremely highly selective transport of secondary amines over tertiary amines (up to a 55:1 ratio). The selective transport of a given solute through the RTIL/membrane system results from the high partitioning of the solute to the liquid membrane phase which, in the case of amines, is rationalized mainly by the formation of a preferential substrate/H−C(2) hydrogen bonding to the imidazolium cation.

Keywords: amines · ionic liquids · liquid membranes · selective transport · separation processes

Introduction

Room-temperature ionic liquids (RTILs), especially those based upon the 1-*n*-alkyl-3-methylimidazolium cation, have attracted growing interest during the last few years.[1, 2] They are nonvolatile, thermally stable, and, depending on the anion and on the alkyl group of the imidazolium cation, the RTIL may solubilize supercritical CO_2 ($scCO_2$), carbonyl compounds, alkyl halides, alcohols, and also transition-metal complexes. Simultaneously, they demonstrate low miscibility with water, alkanes, and dialkyl ethers, and are insoluble in supercritical $scCO_2$.[1, 3] RTILs are emerging as an alternative recyclable, environmentally benign reaction media for chemical transformations,[1, 4] especially for catalysis[5] and biocatalysis.[6] The use of RTIL–$scCO_2$ as a biphasic solvent system for homogeneous catalysis has also been recently demonstrated.[7] RTILs have also been successfully employed as a stationary phase for gas chromatography,[8] in pervaporation,[9] and for the substitution of traditional organic solvents in aqueous organic solvent systems, as well as for selective extraction of metal ions[9a, 10] and for organic solvent/$scCO_2$[7, 11] extractions.

The polarity of four RTILs has been recently assigned and, in the case of 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$), it was considered to be between the values for acetonitrile and methanol.[12]. It is assumed that the 1,3-dialkylimidazolium RTIL is not a statistical aggregate of anions and cations but, instead, a more organized structure containing polar and nonpolar regions, through the formation of weak interactions, mainly involving hydrogen bonds with the C(2)H proton of the imidazolium ring.[1, 13]

Solute extraction and recovery using supported liquid membranes is recognized as one of the most promising membrane-based processes.[14] In a supported liquid membrane system a defined solvent or solvent/carrier solution is immobilized inside the porous structure of a polymeric or ceramic membrane, in such a way that the feed phase, in which the solutes of interest are solubilized, is separated from the receiving phase, where these solutes are transferred to and, eventually, concentrated. This configuration has attracted a great deal of interest, but its industrial application has been hindered by the difficulty in designing supported liquid membranes that exhibit high stability during operation.[15] The use of room-temperature ionic liquids as an immobilized phase in a supporting membrane is particularly interesting due to the nonvolatile character of the RTILs and their

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solubility properties in the surrounding phases, which makes it possible to obtain very stable supported liquid membranes without any observable loss of the RTIL to the atmosphere or the contacting phases.

Our continuing interest in exploring new applications of RTILs[5p,q, 9b] and the potential for development of new separation processes based on supported liquid membranes,[16] prompted us to study the transport of organic compounds between two organic phases using RTILs as a liquid membrane.

Results and Discussion

Bulk (non-supported) ionic liquid membranes: To establish the potential of the RTILs as liquid membranes, we performed preliminary screening transport experiments using U-shaped tubes with the RTIL 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (bmimPF$_6$) as a bulk liquid membrane (0.5 mL) between two diethyl ether phases (3 mL for each side) (Figure 1). A mixture of 1,4-dioxane (**1**), propan-1-ol (**2**), butan-1-ol (**3**), cyclohexanol (**4**), cyclohexanone (**5**), morpholine (**6**), and methylmorpholine (**7**) was added to phase A and the transport of each of these compounds to phase B, through the bmimPF$_6$ liquid membrane, was monitored over time.

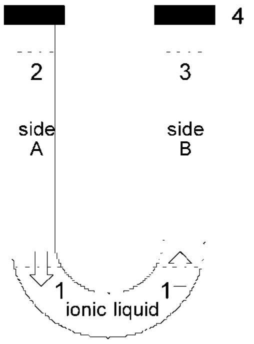

Figure 1. Schematic diagram of the U-tube used for bulk RTIL liquid membrane experiments. 1) Ionic liquid phase (0.5 mL), 2) side A diethyl ether phase (3 mL) containing the mixture of compounds **1**–**7**, 3) side B diethyl ether phase (3 mL), 4) septa.

Figure 2 shows the percentage of recovery of each compound, as detected by GLC in phase B of the U-shaped tube, during the first 6 h of operation.

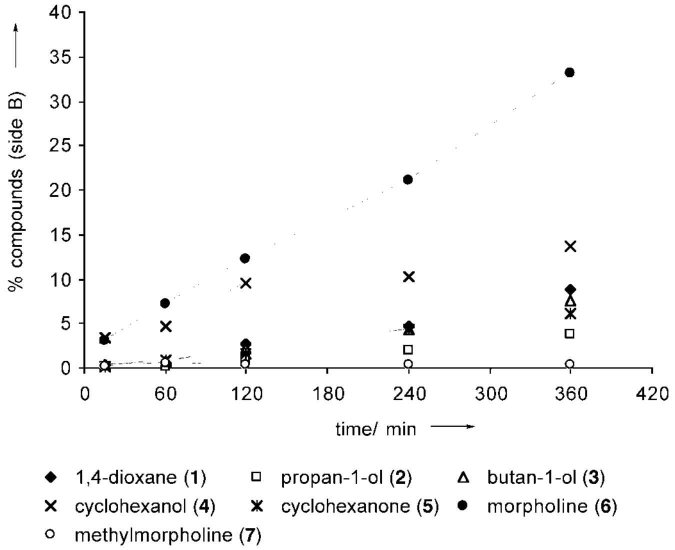

Figure 2. Percentage of recovery of each compound, detected in side B of the U-tube.

Figure 3 displays the percentage of each compound in the bmimPF$_6$ liquid membrane phase, obtained by material balance after determination of the concentration of each compound, in both phases A and B. In all cases tested, solute transport to side B increased during the first 6 h and no significant concentration change was observed in both phases, during the following 24 h.

For the alcohol series **2**, **3**, and **4**, the degree of recovery of each solute increased (3.9, 7.5, and 13.7 %, respectively, after 6 h) with the length of the carbon chain (compound **4** > **3** > **2**). These results are very interesting because in a bulk liquid membrane configuration, in which the diffusion path in the liquid membrane phase is quite long, it is expected that selectivity would be ruled by the diffusivity of each solute in the ionic liquid. Furthermore, in this work, the feed, the receiving, and the liquid membrane phases were not stirred during operation; stirring could lead to a diffusion-controlled process. Therefore, the behavior observed, in which compounds with higher molecular weight are more favorably transported, can only be explained by the importance of the interactions that each solute establishes with the ionic liquid in the membrane phase.

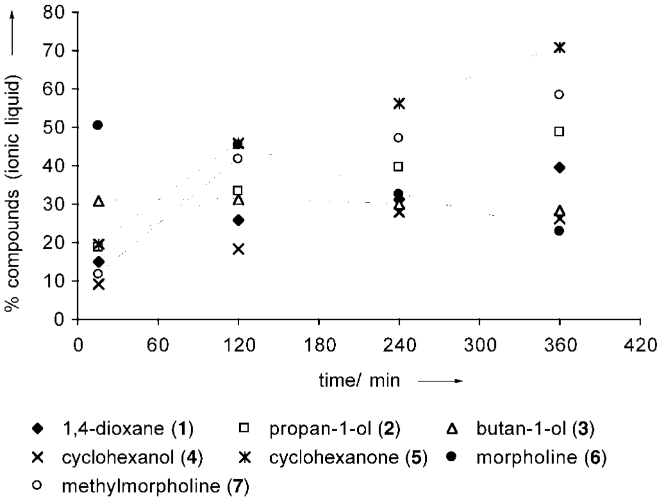

Figure 3. Percentage of each compound in the bmimPF$_6$ liquid membrane phase of the U-tube (relative to the initial amount of each compound in side A).

The transport of the ether **1** is very similar to that of the alcohol **3** (8.8 versus 7.5 % after 6 h) and higher than that of **2** (3.9 % after 6 h) suggesting that the size of the saturated alkyl chain has a stronger effect on the transport than the presence of the hydroxy group. In contrast to the moderate selectivity observed on the examples above, a remarkable difference on the degree of recovery was observed between the amines morpholine (**6**) and methylmorpholine (**7**) (33.1 versus 0.4 % after 6 h). It is also significant that the percentage of each compound solubilized in the bmimPF$_6$ membrane increases slowly over time for all the compounds tested, and that after 6 h a considerable amount of substrate (relative to the initial substrate in phase A) was solubilized in this phase (between 26.4 % for **4** and 70.9 % for **5**). On the other hand, the amount of **6** in the bmimPF$_6$ membrane was extremely high in the beginning (50.3% after 15 min), and then slowly decreased over time (23.1% after 6 h).

These results suggest that the competitive transport mechanism, which results from the overall chemical potential difference between both sides (a mixture of compounds in side A in opposition to diethyl ether in side B), is strongly dependent on the relative affinity of each substrate to the bmimPF$_6$ phase. Importantly, in order to be transported at a high rate, a given solute not only has to be able to interact with the ionic liquid but, also to partition from the ionic liquid phase to the receiving diethyl ether phase. Otherwise, it would accumulate in the RTIL membrane phase. This explains the high degree of recovery observed for morpholine (**6**) which, although it presents a high affinity for the bmimPF$_6$ phase, as can be perceived from its high partitioning to this phase just after 15 min of contact (see Figure 3), it is well recovered to the receiving phase, as can be seen by its decreasing concentration in the membrane phase.

Supported ionic liquid membrane: The above observations, for which a bulk liquid membrane configuration was used, prompted us to study the use of RTILs as new supported liquid membranes for selective transport. The use of supported liquid membranes presents a considerable number of advantages: it permits the operation with an extremely large specific membrane area (membrane area per unit volume) without dispersing the extractant in the feed phase; therefore, phase coalescence and separation is not necessary; extraction and reextraction take place simultaneously, involving a minimal amount of extractant, which is constantly regenerated; additionally, as will be discussed in this work, it is possible to tune the selectivity of the extractant phase to a defined solute by adequate selection of the solid supporting membrane.

The transport studies were performed by using a laboratory-scale cell (2 × 30 mL) (Figure 4). A mixture of compounds was dissolved in diethyl ether in side A of the cell, and side B was filled with diethyl ether. The two compartments were separated by the RTIL immobilized inside the porous structure of a supporting membrane. The transport of each compound to the receiving phase B was monitored over time.

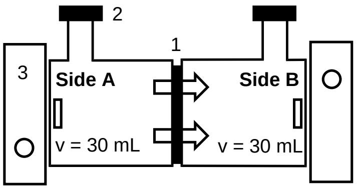

Figure 4. Schematic diagram of the cell used for the supported RTIL liquid membrane experiments; 1) supported liquid membrane (A = 8.5 cm^2); 2) septa; 3) magnetic stirrer.

To understand the effect of the RTIL structure and the supporting membrane, comparative studies were performed by using the mixture of compounds **1**–**7** described above. The following RTILs were evaluated: 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (bmimPF$_6$) and tetrafluoroborate (bmimBF$_4$), 1-*n*-octyl-3-methylimidazolium hexafluorophosphate (C8imPF$_6$) and 1-*n*-decyl-3-methylimidazolium hexafluorophosphate (C10imPF$_6$). The above RTILs were immobilized in the porous structure of different hydrophilic membranes such as polyvinylidene fluoride (PVDF), polyethersulfone (PES), hydrophilic polypropylene (HPP) and nylon, and also in nonhydrophilic polypropylene (NHPP).

Figure 5 presents, as an example, the percentage of recovery for each compound during the first 6 h, using bmimPF$_6$ immobilized in a PVDF membrane. In a blank experiment, using the same PVDF type of membrane without an immobilized ionic liquid, both feed and receiving phases equilibrated for each compound after 30 min. A comparison with the results of the bulk liquid membrane experiment (Figure 2) shows a similar general increase of concentration for each substrate, although some changes on the recovery profiles are noticeable. These changes may be due to the shorter diffusion path involved in the supported liquid membrane configuration, or to different interactions established with the permeating solutes, induced by the chemical nature of the supporting membrane. This latter feature may be explored to improve the separation selectivity for a defined solute mixture.

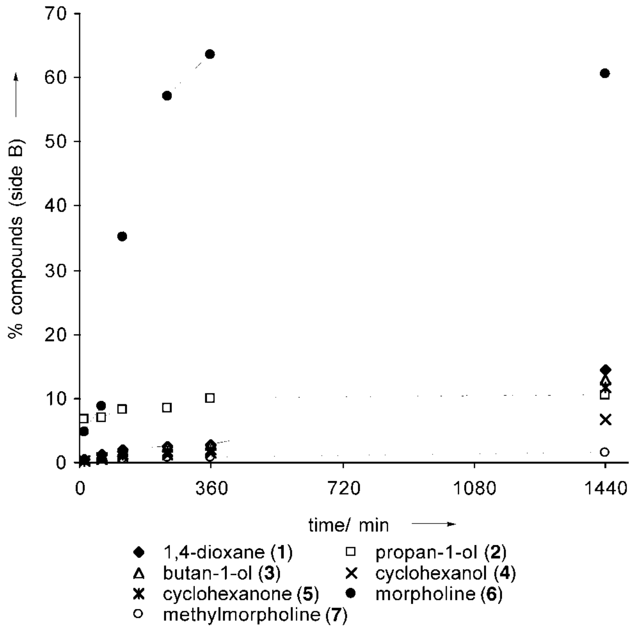

Figure 5. Percentage of recovery of each compound, detected in side B of the cell, using bmimPF$_6$ immobilized in a PVDF membrane.

For the other tested RTIL/supporting membrane combinations, a general increase of the degree of recovery was observed for each substrate during the first 6 h. To simplify data analysis, Table 1 presents the percentage of recovery for each compound after 6 h of operation.

The experiments performed with the same RTIL (bmimPF$_6$) show clearly that the nature of the supporting membrane affects strongly the transport phenomena. Both polypropylene (Table 1, entries 4 and 5) and nylon (Table 1, entry 6) membranes are the ones that render higher transport rates for all the organic compounds studied. As a consequence these liquid membranes exhibit very poor selectivities for the

Table 1. Percentage of recovery for each compound, detected in side B of the cell after 6 h of operation.

Entry	Support[a]	Ionic liquid[b]	**1**[c] [%]	**2** [%]	**3** [%]	**4** [%]	**5** [%]	**6** [%]	**7** [%]	**1**–**7**[d] [%]	Ratio **1:3**	Ratio **2:3:4**	Ratio **4:5**	Ratio **6:7**
1	none	bmimPF$_6$	8.8	3.9	7.5	13.7	6.0	33.1	0.4	10	1:1	1:2:4	2:1	83:1
2	PVDF	bmimPF$_6$	2.8	10.0	2.8	1.5	2.1	63.5	0.8	12	1:1	7:2:1	1:1	79:1
3	PES	bmimPF$_6$	13.0	8.0	11.5	5.0	11.0	33.0	5.0	12	1:1	2:2:1	1:2	7:1
4	HPP	bmimPF$_6$	28.3	6.5	22.4	22.5	27.6	63.1	17.8	27	1:1	1:3:4	1:1	4:1
5	NHPP	bmimPF$_6$	47.5	16.5	39.9	39.9	40.8	41.4	31.8	37	1:1	1:2:2	1:1	1:1
6	nylon	bmimPF$_6$	25.9	37.8	24.5	16.3	20.2	75.5	15.3	31	1:1	2:2:1	1:1	5:1
7	PVDF	bmimBF$_4$	20.0	18.6	19.3	26.4	21.2	57.0	14.0	25	1:1	1:1:1	1:1	4:1
8	nylon	bmimBF$_4$	12.0	7.5	10.0	7.0	7.0	30.0	5.0	11	1:1	1:1:1	1:1	6:1
9	PVDF	C8imPF$_6$	35.7	20.2	34.7	59.5	35.6	44.2	31.8	37	1:1	1:2:3	2:1	1:1
10	nylon	C8imPF$_6$	28.5	12.1	26.2	41.6	26.9	27.9	18.4	26	1:1	1:2:3	2:1	2:1
11	PVDF	C10imPF$_6$	12.0	6.3	11.3	13.6	12.4	27.3	17.9	14	1:1	1:2:2	1:1	2:1

[a] Used abbreviations for the supporting membranes: polyvinylidene fluoride (PVDF), polyethersulfone (PES), hydrophilic polypropylene (HPP), and nonhydrophilic polypropylene (NHPP). [b] Used abbreviations for the ionic liquids (RTIL): 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (bmimPF$_6$), 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (bmimBF$_4$), 1-*n*-octyl-3-methylimidazolium hexafluorophosphate (C8imPF$_6$) and 1-*n*-decyl-3-methylimidazolium hexafluorophosphate (C10imPF$_6$). [c] Legend of organic compounds: 1,4-dioxane (**1**), propan-1-ol (**2**), butan-1-ol (**3**), cyclohexanol (**4**), cyclohexanone (**5**), morpholine (**6**), methylmorpholine (**7**). [d] Overall average percentage of recovery, for all substrates used (**1**–**7**).

different solute combinations. The PVDF support (Table 1, entry 2) is the only membrane that retains the high transport selectivity between amines **6** and **7**, observed during the experiment with bmimPF$_6$ in a bulk liquid membrane. This behavior may be explained by the similarities between the structure of this membrane and perfluorinated solvents, which display a low tendency to undergo van der Waals interactions;[17] in this case, the membrane acts mainly as a solid support without establishing strong interactions with the substrates or with the RTIL.

For the nonhydrophilic polypropylene (NHPP) membrane (Table 1, entry 5) no appreciable selectivity occurs. Furthermore, the selectivity between **4** and **5** is almost negligible for all the membranes tested, except for the most polar membrane, polyethersulfone (PES), which leads to an inversion of selectivity when compared with the bulk liquid membrane experiment (Table 1, entry 3 versus entry 1). For the alcohols **2**–**4** the same inversion of selectivity was observed but in this case for the membranes PVDF, polyethersulfone (PES), and nylon in opposition to the experiments with polypropylene membranes (Table 1, entries 2, 3, and 6 versus entries 4 and 5). In this case the best membrane is again polyvinylidene fluoride (PVDF), because it leads to higher selectivities.

A second set of experiments was performed to understand the effect of the structure of the RTIL used. These experiments were performed with PVDF and nylon membranes because they either lead to the highest selectivity observed (PVDF), or they present the best compromise between selectivity and overall transport efficiency (nylon). The change of anion of the RTIL to the less hydrophobic BF_4^-, promotes an increase of the overall degree of recovery but a drastic decrease of the selectivity, when the PVDF membrane is used (Table 1, entry 7 versus entry 2); for the nylon membrane a decrease of the overall transport was observed, but without an appreciable change of selectivity (Table 1, entry 8 versus entry 6).

With regard to the effect of the alkyl chain of the RTIL, the change of the *n*-butyl-3-methylimidazolium cation to *n*-octyl promotes, for the PVDF membrane, a similar effect to that observed for the substitution of the anion (Table 1, entry 9 versus entry 2), while for the nylon membrane an inversion of selectivity occurred for the alcohol series **2**–**4**, and between cyclohexanol/cyclohexanone **4**/**5** (Table 1, entry 10 versus entry 6). The change of the alkyl chain of the cation to *n*-decyl, provokes a similar reduction of selectivity when using a PVDF membrane (Table 1, entry 11 versus entry 2), but no increase on the overall transport was observed. In this case the behavior observed could also result from a partial solidification of the immobilized RTIL, C10imPF$_6$, on the porous structure of the supporting membrane, which was observed when disassembling the PVDF membrane from the test cell.

Taking into consideration the high selectivity observed for the separation of mixtures comprising secondary and tertiary amines, using bmimPF$_6$ immobilized in PVDF or in nylon supporting membranes, we decided to evaluate the potential of this process for selective amine separation. To accomplish this study we selected different three-component mixtures composed of isomeric primary, secondary, and tertiary amines (M1 and M2), secondary diamine, secondary amine, and tertiary amine (M3). and also two-component mixtures of secondary and tertiary amines for which the difference in boiling points is less than 6 °C (M4–M8).

Table 2 presents the percentage of recovery for each amine after 6 h of operation. For the mixtures containing primary and secondary isomeric amines it can be concluded that selectivity is higher when a nylon support is used, while between secondary and tertiary amines the opposite behavior is observed. Also for the mixture containing the secondary diamine **8c** and the monoamine **9c** a remarkable **9**/**8** ratio of 3:1 was achieved (Table 2, entry 6). This observation is contrast with other results for which a general reduction of selectivity was observed with the increasing length of the alkyl chain of the amines.

The high preference observed for the transport of secondary amines over tertiary amines may result from a preferential interaction with the RTIL bmimPF$_6$. To evaluate this possibility, we performed ^1H NMR experiments based on reported observations where different measurable chemical

Table 2. Percentage of recovery for each amine, detected in side B of the cell after 6 h of operation, using bmimPF$_6$ immobilized in PVDF and nylon membranes.

Entry	Membrane support		Initial mixture	**8** [%]	**9** [%]	**10** [%]	Ratio **9**:**8**	Ratio **9**:**10**
1	PVDF	M1[a]	hexylamine **8a** diisopropylamine **9a** triethylamine **10a**	19.4	94.2	4.1	5:1	23:1
2	nylon	M1[a]	**8a** **9a** **10a**	4.6	89.5	3.8	20:1	24:1
3	PVDF	M2[a]	octylamine **8b** dibutylamine **9b** ethyldiisopropylamine **10b**	19.9	77.3	6.1	4:1	13:1
4	nylon	M2[a]	**8b** **9b** **10b**	12.9	57.6	6.5	5:1	9:1
5	PVDF	M3[a,d]	tetramethylpropanediamine **8c** methylhexylamine **9c** dimethylhexylamine **10c**	28.7	59.3	1.0	2:1	59:1
6	nylon	M3[a,d]	**8c** **9c** **10c**	21.1	54.9	2.3	3:1	24:1
7	PVDF	M4[b,e]	diisopropylamine **9a** triethylamine **10a**		95.2	1.6		60:1
8	PVDF	M4[c,e]	**9a** **10a**		92.9	1.7		55:1
9	nylon	M4[b,e]	**9a** **10a**		92.5	2.8		33:1
10	PVDF	M5[b,f]	*N*-methylbutylamine **9d** triethylamine **10a**		65.4	4.0		16.4
11	nylon	M5[b,f]	**9d** **10a**		82.4	6.4		13:1
12	PVDF	M6[b,g]	*N*-dibutylamine **9b** tripropylamine **10d**		86.0	12.1		7:1
13	nylon	M6[b,g]	**9b** **10d**		82.8	15.3		5:1
14	PVDF	M7[b,g]	*N*-methylbutylamine **9d** dimethylbutylamine **10e**		77.3	10.0		8:1
15	nylon	M7[b,g]	**9d** **10e**		79.8	6.7		12:1
16	PVDF	M8[b,h]	diisopropylethylenodiamine **9e** methyldioctylamine **10f**		62.1	7.8		8:1
17	nylon	M8[b,h]	**9e** **10f**		58.7	15.2		4:1

[a] Initial three-component mixtures in a 1:1:1 volume ratio. [b] Initial two-component mixtures in a **9**/**10** volume ratio of 2:1. [c] Initial two-component mixtures in a **9**/**10** volume ratio of 1:1. [d] Boiling point diference of 6 °C. [e] Boiling point diference of 4 °C. [f] Boiling point diference of 2 °C. [g] Boiling point diference of 3 °C. [h] Boiling point diference of 5 °C.

shifts drifts were described, owing to interaction of the imidazolium ring with the electron-donating group. These interactions are mainly attributed to hydrogen bonding and ring stacking.[13]

Triethylamine (**10a**; TEA) and diisopropylamine (**9a**; DIIPA) were successively added to bmimPF$_6$ in [D$_6$]acetone. Figure 6 shows the observed drift of the chemical shifts ($\Delta\delta$/ppm), for the protons H-C(2), H-C(4), CH$_3$-N(4), and CH$_2$-N(1), on the addition of TEA and DIIPA. Similar profiles were observed by using bmimPF$_6$. In all cases DIIPA promotes a higher drift on the chemical shifts than TEA. This may result from a stronger affinity of the secondary amine DIIPA with bmimPF$_6$. We speculate that this affinity arises from a stronger amine/H-C(2) bonding, which induces the observed changes at the H-C(2) proton through hydrogen bonding and at the other protons by disruption of the initial bmimPF$_6$ ring stacking aggregation, in accordance with a suggested reported model.[13]

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 (p$K_b = 2.95$),[18] over that of TEA (p$K_b = 3.35$)[18], and the steric hindrance of TEA observed on formation of the H-C(2) hydrogen bonding. The reported difference in basicity[18] in aqueous solution for methylmorpholine (p$K_b =$ 6.59) and morpholine (p$K_b =$ 5.64) is in line with the observed transport selectivities. A similar relationship between the selectivity and basicity for the primary and the secondary amines appears to occur, as observed for hexylamine (p$K_b = 10.65$ for octylamine and p$K_b = 10.63$ for pentylamine)[18] and DIIPA. The reduced selectivity observed on amine recovery when using more polar environments—as occurs when the anion BF$_4^-$ or the supporting membranes PES and nylon were employed instead of PF$_6^-$ or bmimPF$_6$, respectively,—may result from an increasing contribution of random nonspecific interactions with other polar groups to the transport mechanism.

Conclusion

This study demonstrates the feasibility of using RTILs as a new kind of solvent in supported liquid membranes for selective transport of organic molecules. Systematic experiments were performed with different mixtures of compounds with representative organic functional groups. From these experiments we concluded that the appropriate combination of selected RTILs and supporting membranes is crucial for achieving good selectivity in a given separation problem. The emergence of a considerable number of new RTILs,[2] and the high variety of commercial supporting membranes will enable the design of RTIL/supporting membrane systems that allow one to obtain the desired selectivity for a specific substrate mixture. The high selectivities obtained in this work for the

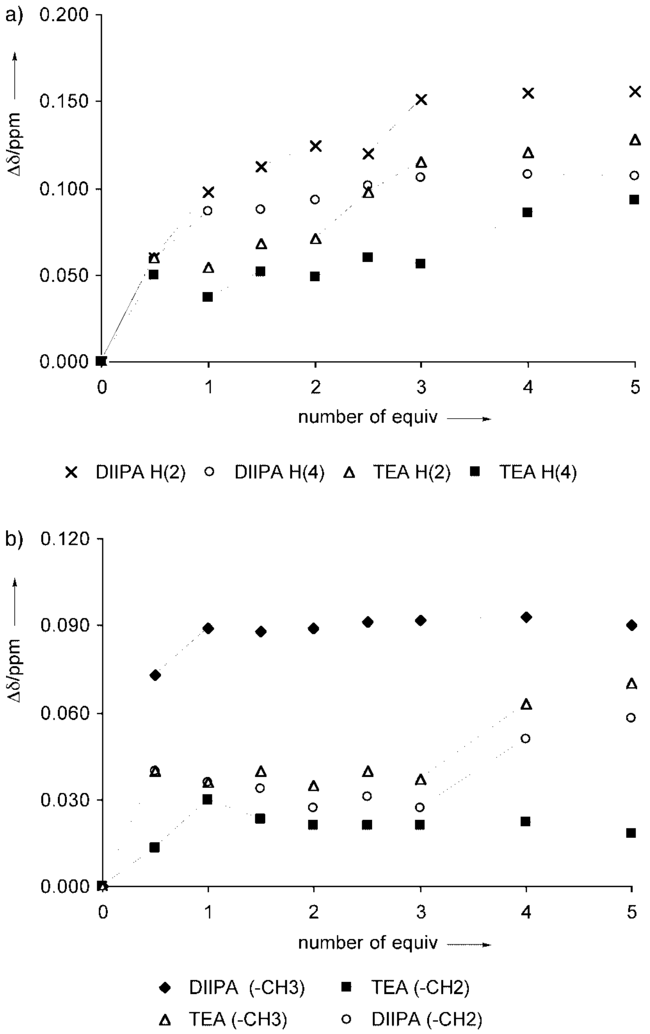

Figure 6. ^{1}H NMR chemical shifts (Δδ/ppm) for bmimPF$_6$ in [D$_6$]acetone as a function of added TEA and DIIPA (equiv): a) H-C(2) and H-C(4) protons; b) CH$_3$-N(4) and -CH$_2$-N(1) protons.

separation of mixtures of secondary and tertiary amines with very similar boiling points demonstrates the potential for the use of this methodology for continuous separation of compounds from complex mixtures—namely the separations difficult to achieve by using traditional distillation methods. To the best of our knowledge there are no other supported liquid membranes capable of separating these organic compounds. Evaporative techniques may be used for the recovery of amines, although methods based on relative volatility of these compounds will not render a high selectivity.

Experimental Section

General remarks: All glassware was oven-dried and cooled in a desiccator (P_2O_5 desiccant) prior to use. Commercial reagents were used as supplied, except for triethylamine, which was distilled from calcium hydride and stored under an argon atmosphere and protected from light. The room-temperature ionic liquids (RTILs) 1-*n*-butyl-3-methylimidazolium hexafluorphosphate (bmimPF$_6$), 1-*n*-butyl-3-methylimidazolium tetrafluorborate (bmimBF$_4$), 1-*n*-octyl-3-methylimidazolium hexafluorphosphate (C8imPF$_6$), 1-*n*-decyl-3-methylimidazolium hexafluorphosphate (C10imPF$_6$) were prepared according to literature methods.[2a, 19] In these studies we used the hydrophilic supporting membranes polyvinylidene fluoride (PVDF) (Gelman Sciences, FP Vericel, pore size 0.45 μm), polyethersulfone (PES) (Gelman Sciences, Metricel Black, pore size 0.45 μm), polypropylene (HPP) (Gelman Sciences, GH Polipro, pore size 0.45 μm), and nylon (Gelman Sciences, Nylaflo, pore size 0.45 μm), and the nonhydrophilic polypropylene (NHPP) (Gelman Sciences, Metricel, pore size 0.1 μm).

^{1}H NMR spectra were recorded on a Bruker AMX 400 spectrometer. Chemical shifts are reported downfield in parts per million (ppm) from a tetramethylsilane reference. Gas liquid chromatography (GLC) was carried out in a Varian Star 3100 Cx gas chromatograph, using He as carrier gas and a capillary column Supelco C315602 SW-10.

General procedure for the bulk ionic liquid membrane experiments: The U-tube (i.d. = 3.5 mm) indicated in Figure 1 was used at room temperature. The ionic liquid bmimPF$_6$ (0.5 mL) was added to the U-tube in vertical position. The organic compounds (200 μL): 1,4-dioxane (**1**; 2.58 mmol), propan-1-ol (**2**; 2.66 mmol), butan-1-ol (**3**; 3.64 mmol), cyclohexanol (**4**; 1.89 mmol), cyclohexanone (**5**; 0.92 mmol), morpholine (**6**; 3.82 mmol), methylmorpholine (**7**; 3.03 mmol), and *n*-dodecane (450 μL, 1.98 mmol) as the internal standard, diluted in diethyl ether (3 mL), were added to side A of the U-tube. *n*-Dodecane (450 μL, 1.98 mmol), diluted in diethyl ether (3 mL), was added to side B of the U-tube. The transport of each compound was monitored by GLC by taking samples from side A and side B of the U-tube at defined time intervals (15, 30, 60, 120, 240 and 360 min), followed by injection into the gas chromatographer (carrier gas flow: 0.9 mL min^{-1}; T(oven) = 60 – 120 °C, 10 °C min^{-1}; T(injector) = 250 °C; T(detector) = 250 °C). The percentage of recovery of each compound was determined by comparison of the area of each of the substrate peaks **1** – **7** (t_R**1** = 0.52, t_R**2** = 0.98, t_R**3** = 1.10, t_R**4** = 6.11, t_R**5** = 3.82, t_R**6** = 2.90, t_R**7** = 1.94 min) with that of *n*-dodecane (t_R = 5.42 min), and referenced to the initial concentrations determined in side A.

General procedure for the supported ionic liquid membrane experiments: The teflon cell indicated in Figure 4 was used throughout these studies. The RTIL was immobilized in the porous structure of the supporting membrane by filtration in vacuo and placed in a metallic net (i.d. 3.29 cm) located between side A (V = 30 mL) and B (V = 30 mL) of the cell. The organic compounds (300 μL): 1,4-dioxane (**1**; 3.87 mmol), propan-1-ol (**2**; 3.99 mmol), butan-1-ol (**3**; 3.28 mmol), cyclohexanol (**4**; 2.84 mmol), cyclohexanone (**5**; 1.38 mmol), morpholine (**6**; 3.44 mmol), methylmorpholine (**7**; 2.73 mmol), and *n*-dodecane (0.5 mL, 2.20 mmol or 1.0 mL, 4.40 mmol) as the internal standard, in diethyl ether (30 mL), were added to side A of the cell. *n*-Dodecane (0.5 or 1.0 mL, 2.20 or 4.40 mmol) in diethyl ether (30 mL) was added to side B of the cell. The transport of each compound **1** – **7** was monitored as described above.

The following quantities were used for the experiments with mixtures of three or two amines (Table 2), dissolved in diethyl ether (30 mL) and containing *n*-decane (400 μL, 2.05 mmol): 3.6 mmol of each amine for entries 1 – 6 and 8 in Table 2; 3.6 mmol of tertiary amines **10** and 7.2 mmol of secondary amines **9** for entries 7 and 9–16 in Table 2. *n*-Decane (400 μL) in diethyl ether (30 mL) was added to side B of the cell. The transport of each amine was monitored as described above by using the following GLC conditions: mixture M1, T(oven) = 80 – 140 °C, 10 °C min^{-1}; T(injector) = 250 °C; T(detector) = 250 °C, t_R**8a** = 3.76, t_R**9a** = 2.38, t_R**10a** = 1.45, *n*-decane (t_R = 0.82 min); mixtures M3 and M8, T(oven) = 80 – 160 °C, 10 °C min^{-1}; T(injector) = 250 °C; T(detector) = 250 °C; M3 t_R**8c** = 2.03, t_R**9c** = 2.45, t_R**10c** = 1.10, *n*-decane (t_R = 0.40 min); M8 t_R**9e** = 2.96, t_R**10f** = 3.65, *n*-decane (t_R = 0.39 min); mixtures M2, M4 – M7, T(oven) = 80 – 150 °C, 10 °C min^{-1}; T(injector) = 250 °C; T(detector) = 250 °C; M2 t_R**8b** = 2.29, t_R**9b** = 0.83, t_R**10b** = 1.43, *n*-decane (t_R = 0.46 min); M4 t_R**9a** = 2.22, t_R**10a** = 0.65, *n*-decane (t_R = 0.47 min); M5 t_R**9d** = 2.71, t_R**10a** = 0.65, *n*-decane (t_R = 0.46); M6 t_R**9b** = 0.86, t_R**10d** = 2.98, *n*-decane (t_R = 0.46 min); M7 t_R**9d** = 2.71, t_R**10e** = 0.92, *n*-decane (t_R = 0.45 min).

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