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Ionic liquids as an efficient bulk membrane for the selective transport of organic compounds

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

The possibility of using ionic liquids (ILs) in bulk (non-supported) liquid membranes for the selective transport of organic molecules has been demonstrated. Recent publications have shown the potential usefulness of ILs in selective transport application and separation processes. In this work, a systematic selective transport study was performed using 1,4-dioxane, 1-propanol, 1-butanol, cyclohexanol, cyclohexanone, morpholine and methylmorpholine as a 7-component mixture of representative organic compounds, and 10 different ILs based on five cation structures such as 1-*n*-alkyl-3-methylimidazolium cation (*n*-butyl and *n*-octyl), 1-*n*-butyl-2,3-dimethylimidazolium cation, 1-(2-hydroxyethyl)-3-methylimidazolium ($[C_2OHmim]^+$), 1-[2-(2-methoxy-ethoxy)-ethyl]-3-methylimidazolium ($[C_5O_2mim]^+$) and tetra-alkyl-dimethylguanidinium cation (alkyl = ethylbutyl and hexyl), combined with PF_6^- and Tf_2N^- anions. These studies allowed us to understand the effect of cation–anion IL structures as novel liquid membranes, and also to conclude that IL polarity seems to be crucial in order to achieve high affinities and selectivities for a specific organic substrate. In general, the use of ILs based on more polar cations containing ether or hydroxyl functional groups increases their affinity for all organic compounds but also reduces the selective transport observed, especially for secondary and tertiary amines. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: ionic liquids; liquid membranes; selective transport; affinity; solute partition

INTRODUCTION

Ionic liquids (ILs), namely the ones involving a 1,3-dialkylimidazolium cation are attracting significant and growing interest as a new media for different applications,[1–21] mainly due non-volatile character and thermally stable.[22–32] Depending on the alkyl group of the imidazolium cation and the anion selected, the IL may solubilise supercritical CO_2 ($scCO_2$), alcohols, carbonyl compounds, alkyl halides and also transition-metal complexes. Simultaneously, the ILs can present low miscibility with dialkyl ethers, alkanes and water, and for many ILs being insoluble in $scCO_2$.[1–21,33–35] As a result of these properties, they are emerging as an alternative recyclable reaction media for several chemical transformations[1–21,36–47] especially for catalysis[37–47] and biocatalysis processes.[48–55] Their use has been successfully extended as a biphasic solvent system for homogeneous catalysis,[37–47,56–58] as a potential stationary phase for gas chromatography and selective gas absorption,[59–71] in dissolution of cellulose,[72–76] in pervaporation[77–79] and for the substitution of traditional organic solvents (OS) in aqueous OS including selective extraction of metal ions[80–89] and for OS–$scCO_2$[90–92] extractions. A specific IL containing a bis-imidazolium cation incorporating a short ethylene glycol spacer was developed and used as the first example of pH dependent partitioning and stripping of mercury from IL/aqueous two-phase systems.[93]

Solute extraction and recovery by using supported liquid membranes is one promising membrane-based process.[94–97] The use of ILs as immobilised phases in supporting membranes is particularly interesting, which we have studied in previous work.[98] In the course of the systematic selective transport study using representative organic compounds, we observed[98,99] an extremely highly selective transport for secondary amines in relation to tertiary amines (ratio of up to 55:1). This high selectivity was due to the occurrence of preferential interactions of the secondary amine with the imidazolium ring, mainly due to the formation of hydrogen bonds with the labile H—C(2) proton. This property was also used to increase the selectivity for the mono-*N*-alkylation of primary amines.[100] It is also assumed that the 1,3-dialkylimidazolium IL is not a statistical aggregate of anions and cations but instead a more organised structure containing polar and non-polar regions due to the formation of weak interactions, mainly as hydrogen bonds with the H—C(2) proton of the imidazolium ring.[101]

In line to our prior study,[98,99] we have continued to explore new applications of the ILs as potential efficient liquid membranes in separation processes. Here, a transport study of some representative organic compounds is presented using different ILs based on imidazolium and guanidinium cations as bulk liquid membranes between two organic phases.

RESULTS AND DISCUSSION

In order to study the potentialities of ILs as liquid membranes, we performed several screening transport experiments using U-shaped tubes with different ILs as a bulk liquid membrane

* *Correspondence to: L. C. Branco, CQFM, Departamento de Engenharia Química e Biológica, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.*
E-mail: carlosafonso@ist.utl.pt; lbranco@dq.fct.unl.pt

a *L. C. Branco, C. A. M. Afonso*
CQFM, Departamento de Engenharia Química e Biológica, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

b *L. Branco, J. Crespo*
REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, Quinta da Torre, 2829-516 Caparica, Portugal

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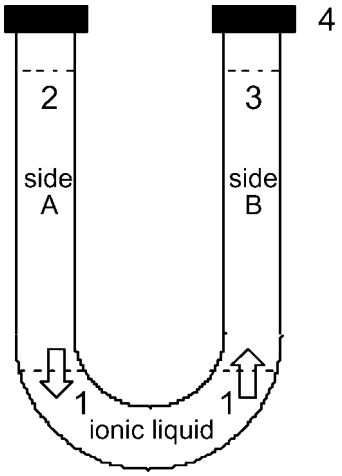

Figure 1. Schematic diagram of the U-shaped tube used for non-supported IL membrane experiments. (1) Ionic liquid phase (0.5 ml), (2) side A: diethyl ether phase (3 ml) containing the mixture of compounds **1**–**7**, (3) side B: diethyl ether phase (3 ml), (4) septa

(0.5 ml) between the two sides of the tube filled with diethyl ether (3 ml for each side) (Fig. 1). For the selective transport study we have selected a mixture of 1,4-dioxane **1**, 1-propanol **2**, 1-butanol **3**, cyclohexanol **4**, cyclohexanone **5**, morpholine **6** and methyl-morpholine **7**, as a 7-model component mixture of representative organic compounds, that were added to the side A and the transport of each compound to the side B through the IL membrane was monitored over time (24 h).

We tested 10 different ILs based on seven cation structures (five imidazolium and one guanidinium cations) such as 1-*n*-alkyl-3-methylimidazolium cation (*n*-butyl; [bmim] and *n*-octyl; [C_8mim]); 1-*n*-butyl-2,3-dimethylimidazolium cation ([bdmim]); 1-(2-hydroxyethyl)-3-methylimidazolium cation ([C_2OHmim]); 1-[2-(2-methoxy-ethoxy)-ethyl]-3-methylimidazolium cation ([C_5O_2mim]) and a more recent class of ILs based on tetra-alkyl dimethylguanidinium cation (butylethyl, [(be)$_2$dmg] and hexyl, [(di-h)$_2$dmg]) combined with PF_6^- and Tf_2N^- anions as shown in Fig. 2. These studies allowed us to study the effect of cation/anion IL structure as novel liquid membranes.

In order to simplify the data analysis, Table 1 presents the percentage of recovery for each compound after 6 h of operation in side B and in the IL phase (in brackets) for 10 ILs tested.

Ionic liquids based on imidazolium cations

In general, the percentage of each compound partitioned to the IL membrane increases mainly during the first hour and after 6 h a considerable amount of each substrate (from 39 to 99%) was partitioned to the IL phase (Table 1). Particular exceptions are 1-butanol **3** (28.4%), cyclohexanol **4** (26.4%), morpholine **6** (23.1%) for [bmim] [PF_6] (entry 1), cyclohexanone **5** (20.2%) and dioxane **1** (5.6%) for [bdmim] [NTf_2] (entry 4). Additionally, the amount of each substrate transported to side B increases more slowly with time, and after 6 h the percentage is still lower than in IL phases (Table 1). However, remarkable differences were observed for different compounds and ILs, which is due to affinity of each substrate in the case of IL or diethyl ether phases.

Interestingly, we observed three exceptions where the concentration of substrate in side B is higher than in the IL phase after 6 h, morpholine **6** for [bmim] [PF_6] (entry 1; 33 *vs.* 23%), dioxane **1** (entry 4; 54 *vs.* 6%) and cyclohexanone **5** (entry 4; 46 *vs.* 20%) for [bdmim] [NTf_2]. In these cases, the concentration of the substrates **1**, **5** and **6** in the IL phase reaches maximum at

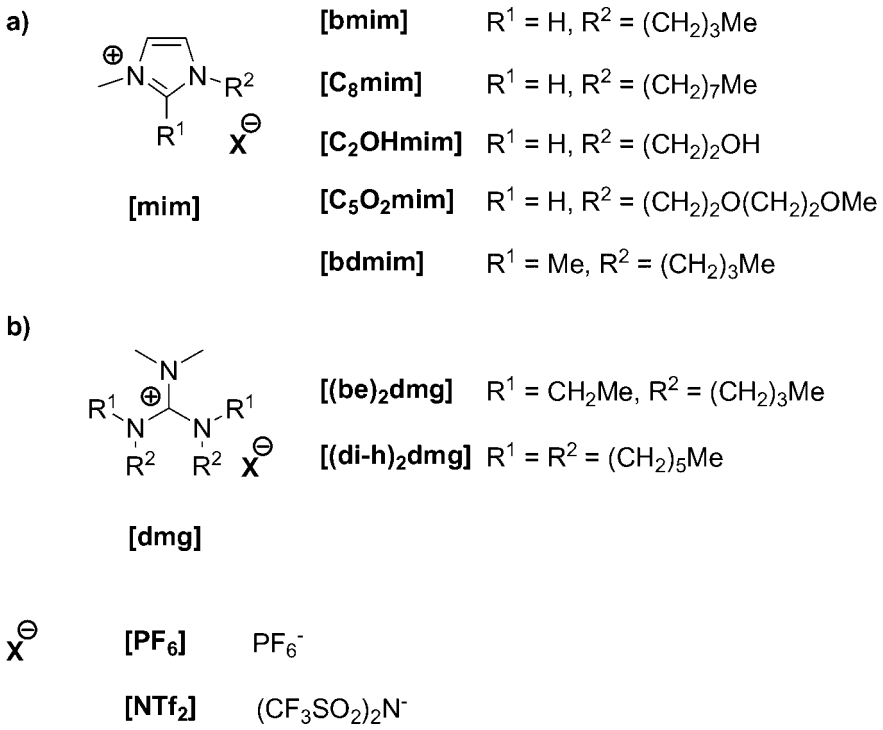

Figure 2. Schematic structure of ionic liquids (ILs) based on (a) methylimidazolium [mim] and (b) guanidinium [dmg] cations used as bulk liquid membranes for the selective transport of organic compounds

Table 1. Percentage of each compound present in side B and in the IL phase (in brackets) of the U-shaped tube (relative to each initial amount localised in side A) using several ILs as liquid membranes after 6 h of operation

Entry	Ionic liquid	% 1[a]	% 2	% 3	% 4	% 5	% 6	% 7	%[b] 1–7	Ratio 1:3	Ratio 2:3:4	Ratio 4:5	Ratio 6:7
1	[bmim] [PF_6]	8.8 (39.4)	3.9 (48.9)	7.5 (28.4)	13.7 (26.4)	6.0 (70.9)	33.1 (23.1)	0.4 (58.3)	10 (42)	1:1 (1:1)	1:2:4 (2:1:1)	2:1 (1:3)	83:1 (1:3)
2	[bmim] [NTf_2]	4.1 (75.0)	4.7 (85.7)	11.5 (73.8)	7.4 (52.0)	9.5 (79.6)	26.5 (58.1)	0.6 (77.5)	9 (72)	1:3 (1:1)	1:3:2 (2:2:1)	1:1 (1:2)	44:1 (1:1)
3	[bdmim] [PF_6]	14.6 (76.7)	1.0 (92.8)	3.5 (89.2)	4.7 (52.3)	0.7 (97.1)	3.8 (76.8)	22.3 (48.5)	7 (76)	4:1 (1:1)	1:4:4 (2:2:1)	7:1 (1:2)	1:6 2:1)
4	[bdmim] [NTf_2]	53.9 (5.6)	24.5 (55.3)	36.3 (44.7)	20.6 (66.9)	45.9 (20.2)	25.0 (57.5)	25.8 (56.7)	33 (44)	2:1 (1:8)	1:2:1 (1:1:1)	1:2 (3:1)	1:1 (1:1)
5	[C_8mim] [PF_6]	26.1 (53.2)	14.7 (69.0)	10.1 (79.5)	15.9 (67.4)	19.5 (62.5)	14.6 (54.2)	12.3 (66.3)	16 (65)	3:1 (1:2)	2:1:2 (1:1:1)	1:1 (1:1)	1:1 (1:1)
6	[C_2OHmim] [PF_6]	8.3 (67.4)	5.8 (67.6)	2.4 (74.1)	3.2 (69.4)	1.5 (70.9)	1.9 (76.0)	0.3 (99.0)	3 (75)	3:1 (1:1)	2:1:1 (1:1:1)	2:1 (1:1)	6:1 (1:1)
7	[C_5O_2mim] [PF_6]	3.6 (70.0)	2.3 (79.4)	4.2 (74.6)	3.2 (87.8)	18.1 (68.1)	5.7 (64.9)	0.01 (99.9)	5 (78)	1:1 (1:1)	1:2:1 (1:1:1)	1:6 (1:1)	570:1 (1:2)
8	[(di-h)$_2$ dmg] [NTf_2]	51.0 (10.2)	23.2 (45.2)	21.0 (64.0)	42.6 (13.8)	39.7 (18.7)	36.8 (11.7)	45.6 (8.4)	37 (24)	2:1 (1:6)	1:1:2 (1:1:3)	1:1 (1:1)	1:1 (1:1)
9	[(be)$_2$ dmg] [PF_6]	33.9 (29.3)	23.7 (48.7)	20.9 (55.4)	33.0 (34.7)	37.2 (27.0)	65.1 (2.6)	20.7 (54.8)	33 (36)	2:1 (1:2)	1:1:1 (2:2:1)	1:1 (1:1)	3:1 (1:21)
10	[(be)$_2$ dmg] [NTf_2]	19.2 (56.7)	21.5 (54.6)	18.6 (64.4)	25.4 (38.1)	22.1 (50.7)	41.9 (14.4)	17.6 (45.6)	24 (46)	1:1 (1:1)	1:1:1 (2:2:1)	1:1 (1:1)	2:1 (1:3)

[a] Legend of organic compounds: **1** 1,4-dioxane; **2** 1-propanol; **3** 1-butanol; **4** cyclohexanol; **5** cyclohexanone; **6** morpholine; **7** methylmorpholine; (in brackets is provided the values in ionic liquid phase).

[b] Percentage of the total substrates transported to the side B and in the IL phase (in brackets) relative to the total initial amounts localised on side A.

20–30 min and then slowly decreases over time. In clear contrast, there are other cases where the substrate presents a high affinity to IL phase and the transport occurs slowly to the side B (or is almost absent ($\leq$0.7%)) such as in the case of cyclohexanone **5** for [bdmim] [PF_6] (entry 3; 0.7 *vs*. 97%), methylmorpholine **7** for [bmim] [PF_6] (entry 1; 0.4 *vs*. 58%), [bmim] [NTf_2] (entry 2; 0.6 *vs*. 78%), [C_2OHmim] [PF_6] (entry 6; 0.3 *vs*. 99.0%) and [C_5O_2mim] [PF_6] (entry 7; 0.01 *vs*. 99.9%).

For the alcohol series **2**–**4**, the degree of recovery of each substrate in side B increased with the length of the carbon chain for [bmim] [PF_6] (entry 1; 3.9, 7.5 and 13.7%), [bdmim] [PF_6] (entry 3; 1.0, 3.5 and 4.7%). For ILs [bmim] [NTf_2] (entry 2), [bdmim] [NTf_2] (entry 4) and [C_5O_2mim] [PF_6] (entry 7), the recovery is higher for 1-butanol **3** than for cyclohexanol **4**. Taking in consideration that in this bulk liquid membrane the diffusion path in the IL membrane phase is long (approx. 2.5 cm), and each phase was not stirred, it is expected that selectivity would be determined by diffusion of each compound in the IL, which implies faster transport for smaller solutes. However, the observed behaviour for many cases (more favourable transport for the higher molecular weight compounds) can be rationalised by the importance of the interactions that each compound establishes with the IL phase.

The IL [bdmim] [PF_6] possesses higher affinity for dioxane (76.7%), propanol (92.8%), butanol (89.2%), morpholine (76.8%) and cyclohexanone (97.1%) while the more polar IL [C_5O_2mim] [PF_6] has higher affinity for cyclohexanol (87.8%) and an enormous affinity for methylmorpholine (99.9%), a fact we again witness in the case of the IL [C_2OHmim] [PF_6]. In general, we observed that the overall affinity of organic compounds (**1**–**7**) to the IL phases increases with the polarity of the IL (78% for [C_5O_2mim] [PF_6] and 75% for [C_2OHmim] [PF_6] *vs*. 42% for [bmim] [PF_6]). For example a remarkable difference on the transport of methylmorpholine to the IL phase was observed after 15 min of operation for [bmim] [PF_6] (11.8%), [C_5O_2mim] [PF_6] (99.0%) and [C_2OHmim] [PF_6] (98.0%).

When we have modified the cation structure of $[bmim]^+$ to $[C_8mim]^+$ or to $[bdmim]^+$ a considerable increase (2 $\times$ higher) in affinity for all organic compounds occurred, except for methylmorpholine in the case of [bdmim] [PF_6] and for cyclohexanone in the case of [C_8mim] [PF_6]. The higher affinity for all organic compounds, except cyclohexanone is facilitated when we have used ILs based on more polar cations such as [C_2OHmim] [PF_6] and [C_5O_2mim] [PF_6].

In relation to the anion effect, for $[bmim]^+$ by changing the [PF_6] to [NTf_2], an increase affinity for all organic compounds was observed. In contrast, we observed that in the case of $[bdmim]^+$ cation the same modification of anion ([PF_6] to [NTf_2]) provoked a reduced affinity for all organic compounds (especially in the case of dioxane), except for cyclohexanol and methylmorpholine.

Figure 3 presents the percentage of morpholine **6** and methylmorpholine **7** (Fig. 3a–d) in the side B (receiving phase) and in the IL phase of several ILs, obtained by material mass balance after determination of the concentration of each compound in both sides A and B for the different ILs.

In the case of the amines morpholine and methylmorpholine, a remarkable selectivity was observed for ILs [bmim] [PF_6] (entry 1; 83:1) and [bmim] [NTf_2] (entry 2; 44:1). In contrast, when we introduced a methyl group in position 2 of imidazole ring, the selectivity was almost negligible for [bdmim] [NTf_2] (entry 4; 1:1) or significantly inverted for [bdmim] [PF_6] (entry 3; 1:6).

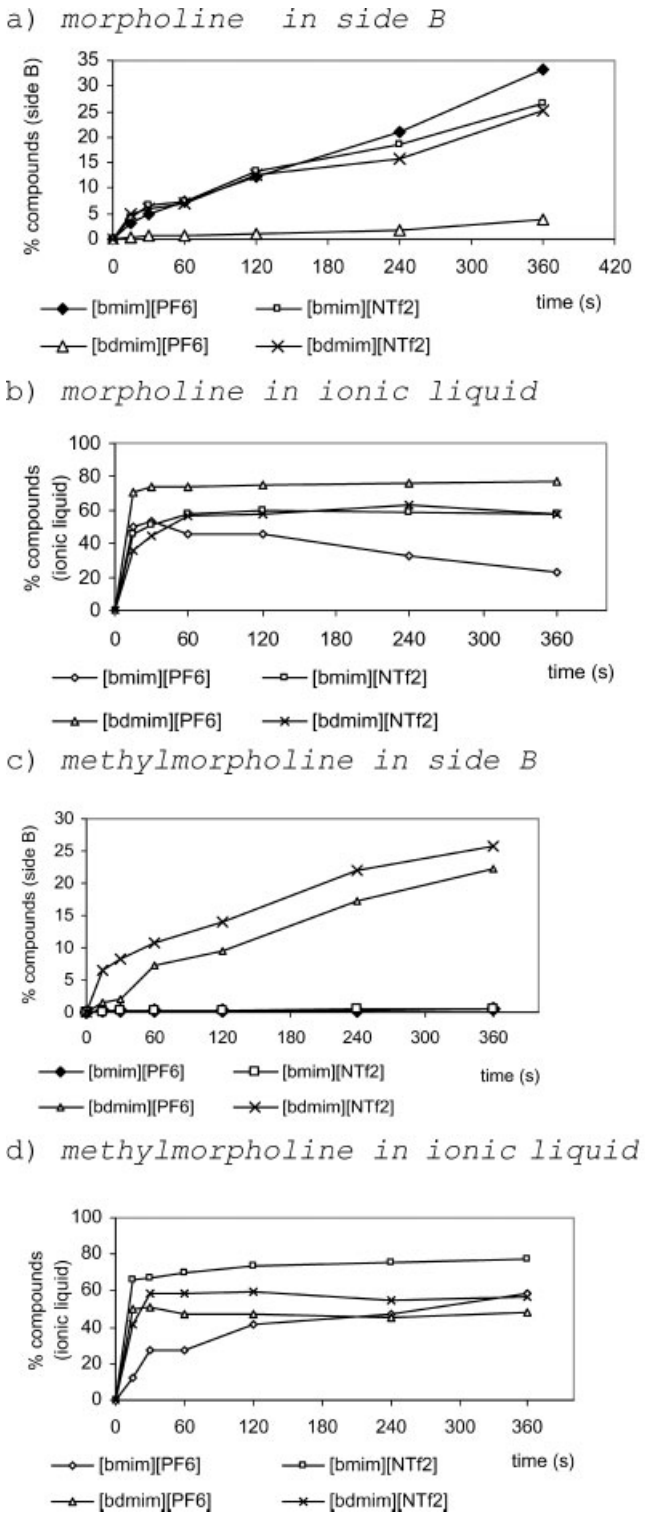

Figure 3. Percentage of each compound in the side B (receiving phase) and in the ionic liquid phase for several ILs membranes of the U-shaped tube (relative to the initial amount of each compound in side A). Legend of figures: (a) morpholine (in side B); (b) morpholine (in ionic liquid phase); (c) methylmorpholine (in side B); (d) methylmorpholine (in ionic liquid phase)

Additionally, the amount of tertiary amine methylmorpholine **7** transported to side B of the U-shaped tube is almost insignificant for the ILs [bmim] [PF_6] (entry 1; 0.4%), [bmim] [NTf_2] (entry 2; 0.6%), [C_2OHmim] [PF_6] (entry 6; 0.3%) and [C_5O_2mim] [PF_6] (entry 7; 0.01%).

Ionic liquids based on guanidinium cations

Analysing the results in Table 1 of the recovery for each compound detected in side B of the U-shaped tube after 6 h of operation, it is clear that guanidinium ILs allowed a significant improve in the overall transport of organic compounds (**1**–**7**) compared with imidazolium ILs.

In the case of IL [$(di\text{-}h)_2$dmg] [NTf_2] no significant selectivity was observed. After 6 h a high affinity of 1-propanol and 1-butanol to the IL phase (entry 8; 45.2 and 64%, respectively) was observed which is in contrast to the lowest percentages of the others substrates to IL phase (lower than 20%).

Using the IL [$(di\text{-}h)_2$dmg] [NTf_2] as liquid membrane was possible the best transport percentages for cyclohexanol (42.6%) and methylmorpholine (45.6%).

The change of guanidinium cation structure from [$(di\text{-}h)_2$dmg] (symmetric structure) to [$(be)_2$dmg] (no symmetric structure) provoked a reduction in the overall transport of organic compounds to side B after 6 h of operation, in particular in the case of 1,4-dioxane and cyclohexanol.

In the same line observed for IL [bmim] (entries 1 and 2) using [$(be)_2$dmg] as liquid membrane (entries 9 and 10) provided some selectivity for amines (morpholine **6**:methylmorpholine **7**). Additionally, the amount of secondary amine morpholine **6** transported to side B of the U-shaped tube is the highest for the ILs [$(be)_2$dmg] [PF_6] (entry 9; 65.1%), [$(be)_2$dmg] [NTf_2] (entry 10; 41.9%).

Concerning to the anion effect for the [$(be)_2$dmg] cation, by changing the anion [PF_6] to [NTf_2], no appreciable change of the selectivity as well as a slight reduction of overall transport (33 *vs.* 24%) were observed for all organic compounds.

CONCLUSIONS

These studies demonstrate that ILs are potential media as liquid membranes for the selective transport of organic molecules. We performed a systematic study with different mixtures of compounds of representative organic functional groups and several ILs that allowed us to discuss the effect of the cation and the anion on the IL behaviour as a novel liquid membrane. We can conclude that the appropriate combination of cation and anion is crucial to achieve good affinities and selectivity for a specific organic substrate.

In general, the use of more polar imidazolium ILs increases the affinity and subsequent solubility capacity for all organic compounds, but also reduces the selective transport observed, especially for secondary and tertiary amines. The guanidinium ILs allowed the best overall transport percentages for all organic compounds. The experiments performed show clearly that the nature of the structure of both the cation and the anion affect strongly the selective transport phenomena.

The high preference observed for the transport of secondary amines in comparison with tertiary amines in ILs based on the $[bmim]^+$ cation results from a high partitioning of the solute to the liquid membrane phase that is rationalised mainly by the

formation of preferential substrate/H—C(2) hydrogen bonding on the imidazolium cation.[98,99] This rationalisation is also consistent with the inversion of selectivity observed for ILs based on $[bdmim]^+$ cation structure, where the H—C(2) proton is absent.

It is also clear that to achieve a high transport and selectivity of a given solute, the combination of the affinity of each solute to the IL and subsequent partition to the receiving phase (side B) is absolutely crucial. In fact, we observed that certain solutes are almost instantaneously partitioned to the IL phase but they are not transported further to the receiving phase (e.g. methylmorpholine for $[C_2OHmim]$ $[PF_6]$ and $[C_5O_2mim]$ $[PF_6]$) and others that are efficiently transported to the receiving phase (e.g. dioxane for [bdmim] $[NTf_2]$ and $[(di\text{-}h)_2dmg]$ $[NTf_2]$ and morpholine for $[(be)_2dmg]$ $[PF_6]$). In terms of selectivity, it was observed in general a higher, and in some cases inverted, selectivity for the solutes in the receiving phase than in the IL phase, which demonstrates the importance of the second partition step (IL to side B) for the overall solute transport. This means that the nature of the IL and of the OS in the feed (side A) and in the receiving phase (side B) play an important role in the transport phenomena. From this study, it is also clear that to achieve the desired transport for a specific target solute, some prior two-phase partition equilibrium and transport studies should be performed by combination of ILs and immiscible organic or fluorous solvents. In this context, the emergence of a considerable number of new ILs,[1–21] including commercial available ones, and tailored ILs if required,[93,102–104] will make it possible to achieve the desired selectivity.

EXPERIMENTAL SECTION

All glassware was oven dried and cooled in a desiccator (P_2O_5 desiccant) prior to use. Commercially supplied reagents were used as supplied.

The imidazolium ILs 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [bmim] $[PF_6]$, 1-*n*-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim] $[NTf_2]$, 1-*n*-octyl-3-methylimidazolium hexafluorophosphate $[C_8mim]$ $[PF_6]$, 1-*n*-butyl-2,3-dimethylimidazolium hexafluorophosphate [bdmim] $[PF_6]$, 1-*n*-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide [bdmim] $[NTf_2]$, 1-(2-hydroxyethyl)-3-methylimidazolium hexafluorophosphate $[C_2OHmim]$ $[PF_6]$ and 1-[2-(2-methoxy-ethoxy)-ethyl]-3-methylimidazolium hexafluorophosphate $[C_5O_2mim]$ $[PF_6]$ were prepared following reported procedures.[105–108] The guanidinium ILs tetra-hexyl-dimethylguanidinium bis(trifluoromethylsulfonyl)imide $[(di\text{-}h)_2dmg]$ $[NTf_2]$, tetra-butylethyl-dimethylguanidinium hexafluorophosphate $[(be)_2dmg]$ $[PF_6]$and tetra-butylethyl-dimethylguanidinium bis(trifluoromethylsulfonyl)imide $[(be)_2dmg]$ $[NTf_2]$ were prepared as described elsewhere.[109] Gas liquid chromatography (GLC) was carried out on a Varian Star 3100 Cx gas chromatograph, using He as carrier gas and capillary column Supelco C315602 SW-10. The bulk IL membrane experiments were performed following the conditions described elsewhere.[98]

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