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Highly Selective Transport of Organic Compounds by Using Supported Liquid Membranes Based on Ionic Liquids**

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The selective separation of organic compounds is a critical issue in the chemical industry. In case of readily crystallized molecules, selective crystallization is the most practical method for selective separation, whereas for solutes that are liquid at room temperature, separation by fractional distillation, solvent extraction, or chromatographic methods are more convenient. Some of the above-mentioned methods are technically demanding, involve considerable energy costs, and/or result in large amounts of waste solvents. Membranes, defined as permeable and selective barriers between two phases, have been successfully applied in a large diversity of separation processes, including bioseparations, in which classical separation methods are less convenient, undesirable or even not applicable. The reason for the successful use of membrane-based separation processes stems from the fact

that these processes have a high energy efficiency, can be used under moderate temperature and pressure conditions, do not require any additional separating agents or adjuvants, and therefore they are regarded as environmentally friendly.^[1] Solute extraction and recovery by using supported liquid membranes is recognized as one of the most promising membrane-based processes. 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, which separates the feed phase (in which the solutes of interest are solubilized) from the receiving phase (in which these solutes will be transferred and, eventually, concentrated). This configuration has attracted a great deal of interest because the amount of solvent/carrier needed is minimal, the solvent/carrier is continuously regenerated as a result of solute transport to the receiving phase, and loss of the solvent/carrier phase is negligible if an appropriate supported liquid membrane is designed.^[2] The use of a room-temperature ionic liquid (RTIL) as an immobilized phase in the supporting membrane between two organic phases in the feed and the receiving compartments is particularly interesting owing to the nonvolatile character of RTILs and their solubility in the surrounding phases, which allows very stable supported liquid membranes to be obtained without any observable loss of the RTIL to the atmosphere or the contacting phases. Herein we show the potential for continuous separation of organic compounds based on the selective transport through supported liquid membranes that contain RTILs.

RTILs that involve a 1,3-dialkylimidazolium cation are attracting increasing interest as new media, mainly because of the advantage of being nonvolatile. Depending on the anion and on the alkyl group of the imidazolium cation, the RTIL can solubilize supercritical CO_2 (scCO_2), a large range of polar and nonpolar organic compounds, and also transition-metal complexes. Simultaneously, they have low miscibility with water, alkanes, and dialkyl ethers^[3] and are insoluble in scCO_2 .^[4] As a result of these properties, they are emerging as an alternative recyclable, environmentally benign, reaction medium for chemical transformations, including transition-metal catalysis^[3] and biocatalysis.^[3f, 5] Their use has also been successfully extended as a potential stationary phase for gas chromatography,^[6] in pervaporation,^[7] and for the substitution of traditional organic solvents (OS) in aqueous–OS^[7a, 8] and OS– scCO_2 biphasic extractions.^[4, 9] It is assumed that the 1,3-dialkylimidazolium RTIL are not a statistical aggregate of anions and cations, but instead a more organized structure that contains polar and nonpolar regions as a result of the formation of weak interactions, mainly as hydrogen bonds, with 2-H of the imidazolium ring.^[10] The above information prompted us to study the potential of using RTIL in supported liquid membranes for selective separation processes.

To illustrate the concept, and as a result of transport studies with representative organic functional compounds, we used a mixture of the organic isomeric amines hexylamine, diisopropylamine, and triethylamine (1:1:1 molar ratio) in diethyl ether in side A of the cell (Figure 1). The two sides of the cell were separated by the RTIL 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($[\text{bmim}][\text{PF}_6]$) immobilized in the por-

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[**] This work was supported by the European Commission (contract QLK3-CT-1999-01213) and the Fundação para a Ciência e Tecnologia (project PRAXIS/C/QUI/10069/98). We also acknowledge Raquel Fortunato for the technical support with the membranes and for helpful discussions.

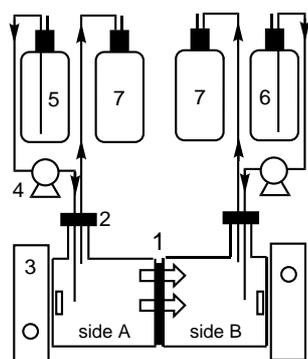


Figure 1. Scheme of the cell used in batch (without pumps) and continuous systems: volume of each side of the cell = 30 mL; 1) supported liquid membrane ($A = 8.5 \text{ cm}^2$); 2) septa (without pumps) or connection to the pumps; 3) magnetic stirrer; 4) pumps; 5) feed solution containing the solutes; 6) receiving solution containing fresh solvent; 7) collection bottle.

ous structure of a polyvinylidene fluoride (PVDF) hydrophilic membrane. Diethyl ether was used as the receiving phase in compartment B. The transport of the primary, secondary, and tertiary amines to compartment B was then monitored (Figure 2).

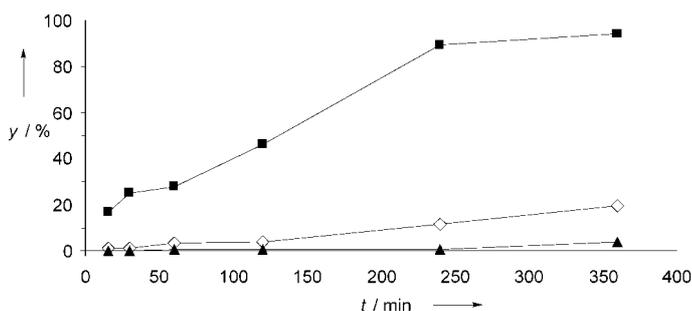


Figure 2. Percentage of recovery of each amine in compartment B of the cell, for batch operation. \diamond hexylamine; \blacksquare diisopropylamine (DIIPA); \blacktriangle triethylamine (TEA).

We observed a stronger selectivity for diisopropylamine transport than for hexylamine and triethylamine. We also observed by ^1H NMR spectroscopic analysis that the addition of diisopropylamine to neat $[\text{bmim}][\text{PF}_6]$ promotes a larger shift of the peaks for the 1-*n*-butyl-3-methylimidazolium cation than of those for triethylamine, which suggests that the high transport selectivity arises from the higher affinity of the secondary amine for $[\text{bmim}][\text{PF}_6]$. This affinity probably arises from the combination of the higher basicity of DIIPA than that of TEA and the steric hindrance of TEA on approach to the $[\text{bmim}]$ cation. Diffusivity does not play a major role in the selective transport of these amines because they have the same molecular weight and their different geometry and dipolar moment cannot explain such large differences in their selective transport through the RTIL supported liquid membrane.

As a result of this batch experiment, we turned our attention to the possibility of performing continuous separations. To illustrate the potential of this approach, we tested a

mixture of DIIPA (b.p. = 84°C) and TEA (b.p. = 89°C) as a separation case study of secondary and tertiary amines with similar boiling points. The cell presented in Figure 1 was used by circulating an equimolar mixture of DIIPA and TEA in diethyl ether in side A and fresh diethyl ether in side B. Figure 3 presents the observed transport selectivities at the

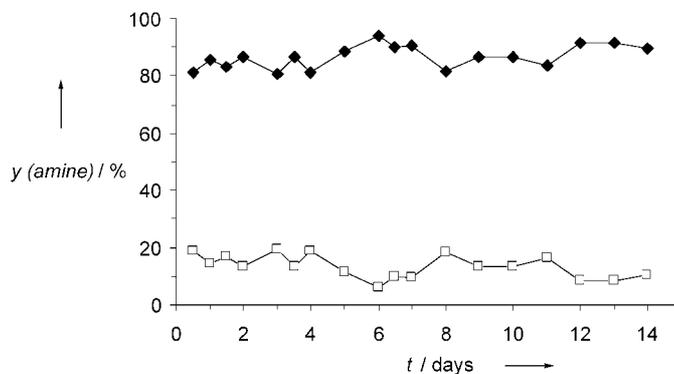


Figure 3. Relative percentage of each amine in the receiving stream obtained for eighteen collecting samples (12-h period), determined by GLC during 14 days of continuous operation. \blacklozenge diisopropylamine; \square triethylamine.

outlet of compartment B during 14 days of continuous operation. The observed DIIPA/TEA ratios in the collected samples were higher than 80:20 under optimized conditions, and a moderate decrease was only observed for the periods during which undesired variations of the flow rates occurred. Importantly, the transport selectivity did not decrease during the entire extended period of operation, which confirms the stable character of the supported liquid membrane system. The stability of the $[\text{bmim}][\text{PF}_6]$ -supported membrane suggests that longer continuous operation periods are feasible. The overall percentage of recovery (based on the 14 days of continuous operation) was 84.7% for DIIPA and 14.9% for TEA. Notably, the mass flux of DIIPA was $1070.6 \text{ g of DIIPA}/(\text{m}^2 \text{ of membrane hour})$, which can be considered an excellent transport rate. Interestingly, the total amount of $[\text{bmim}][\text{PF}_6]$ used in the supported liquid membrane was only $202 \text{ g of } [\text{bmim}][\text{PF}_6]/(\text{m}^2 \text{ of membrane})$. As the solutes transported through the supported liquid membrane are continuously recovered in the receiving solution, the RTIL used is regenerated and may be effective for prolonged operation. To the best of our knowledge, there are no other supported liquid membranes that are able to separate these organic compounds. The system presented herein is particularly interesting because it involves the use of a supported liquid membrane with a high operating stability and an excellent selectivity for the recovery of the target compound.

The model system presented herein illustrates the potential for the continuous highly selective separation of mixtures of isomeric organic compounds that are structurally similar and have close boiling points by using the RTIL $[\text{bmim}][\text{PF}_6]$ in a supported liquid membrane. This separation process is feasible under simple technical conditions, and proved to be stable even during long periods of operation. This method

seems particularly appealing for large-scale operations and for different substrates; with the emergence of a considerable number of new RTILs,^[3, 11] it should be possible to design RTILs with high selectivity for specific substrates. The possibility of using nonpolar solvents with high boiling points or water instead of diethyl ether, and supported RTIL in hollow-fiber membranes will allow this technology to reinforce its environmentally benign character and become attractive for industrial application.

Experimental Section

For the batch studies, the cell indicated in Figure 1 was used without pumps. The ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) was immobilized in the porous structure of a polyvinylidene fluoride (PVDF) hydrophilic membrane (Gelman Sciences, FP Vericel, pore size 0.45 μm) by filtration in vacuo and placed in a metallic net (i.d. 1.65 cm) located between side A (*V* = 30 mL) and side B (*V* = 30 mL) of the cell. The amines (1:1 molar mixture) hexylamine (470 μL), DIIPA, (500 μL) and TEA (500 μL), and *n*-decane (400 μL; internal standard) in diethyl ether (30 mL) were added to side A of the cell. *n*-Decane (400 μL; internal standard) was added to diethyl ether (30 mL) in side B of the cell. The transport of amines to side B at room temperature was monitored by GLC by taking samples from side A and B of the cell at defined time intervals (15, 30, 60, 120, 240, 360 min). The recovery of each amine was determined by comparison of the areas of the peaks of each amine with those of *n*-decane and relative to the areas initially observed in side A.

For continuous operation conditions, the cell indicated in the Figure 1 was used, with each side of the cell connected to a piston pump (FMI lab pump, model QSY) to promote the circulation in each side. The RTIL [bmim][PF₆] was immobilized as indicated above. The amines (1:1 molar mixture) DIIPA (100 mL) and TEA (100 mL) in diethyl ether (5 L) were circulated with a flow rate of 1 mL/min in side A of the cell. Diethyl ether (5 L) was circulated with a flow rate of 1 mL min⁻¹ in side B of the cell. Both solutions were renewed every 2 days. The transport of each amine to side B was monitored by sequentially collecting samples from the outlet tube of side B every 12 h. During the 14 days of continuous operation, 23 samples were collected with a total volume of 20410 mL. The DIIPA/TEA ratio was determined for each sample by GLC. Eighteen samples (15460 mL) were fractionally distilled to afford a mixture of DIIPA/TEA (250 mL; 89.2:10.8, determined by GLC); ¹H and ¹³C NMR spectral data were identical to those of authentic samples. The distilled diethyl ether fraction and the remaining six samples contained a mixture of DIIPA/TEA (142.2 mL (81.6:18.4) and 105.7 mL (80.9:19.1), respectively, ratio determined by GLC analysis with *n*-decane as internal standard).

Received: January 25, 2002 [Z18583]

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Lewis Acid Controlled Regioselective 1,2 and 1,4 Reaction of α,β -Unsaturated Carbonyl Compounds with Ti^{IV} Enolates Derived from α -Diazo β -Keto Carbonyl Compounds**

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The addition of nucleophiles to α,β -unsaturated carbonyl compounds is a fundamental transformation in organic synthesis. Since there are two reaction sites in the α,β -unsaturated carbonyl functional group, this addition reaction can only be of practical synthetic utility in organic synthesis if one

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[**] The project is generously supported by the Natural Science Foundation of China (Grant Nos. 29972002, 20172002) and Trans-Century Training Program Foundation for the Talents by the Ministry of Education of China.

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