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Journal of Membrane Science 307 (2008) 233–238

journal of MEMBRANE SCIENCE

www.elsevier.com/locate/memsci

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

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Received 6 June 2007; received in revised form 13 September 2007; accepted 15 September 2007
Available online 21 September 2007

Abstract

Previously, we reported the selective simultaneous separation of the substrates and products of a transesterification reaction (vinyl butyrate, 1-butanol, butyl butyrate, and butyric acid) through supported liquid membranes (SLMs) based on two ionic liquids (ILs): 1-butyl-3-methylimidazolium hexafluorophosphate, $[\text{bmim}^+][\text{PF}_6{}^-]$, and 1-octyl-3-methylimidazolium hexafluorophosphate, $[\text{omim}^+][\text{PF}_6{}^-]$. The significant differences observed in the selectivity values, attributed to the different nature of the ionic liquid phase used, led us to further investigate this matter.

In this work, six ionic liquids were tested as liquid phase in SLMs for the selective separation of vinyl butyrate, 1-butanol, butyl butyrate, and butyric acid. The influence of the IL as liquid phase in the resulting SLMs was analyzed measuring the values of permeability for each organic compound through the SLMs. In all cases, significant permeability differences between the organic compounds were obtained. The hydrophilic/hydrophobic character of the IL used, measured by the octanol–water partition coefficients (K_{ow}), was found to be a key parameter for the selective behaviour of the SLM. It was observed that a decrease in the K_{ow} of the ionic liquid resulted in a higher separation efficiency of the resulting SLM.

Keywords: Ionic liquids; Supported liquid membranes; Membrane transport; Transesterification reaction; Octanol–water partition coefficient

1. Introduction

Supported liquid membranes (SLM) is a novel and promising technique for the selective separation of organic compounds involved in pharmaceutical and fine chemical synthesis [1–6]. Their main advantages over conventional solvent extraction processes, such as simplicity of operation or economical utilization, are lessened by their well-known disadvantages relating to stability and lifetime [7,8], which are too low to ensure feasible commercial application. For this reason, the characteristics and application of ILs, which can be used as solvents capable of stabilizing SLM, have received growing attention during recent years [9–11]. Ionic liquids, which are liquid close to room temperature, normally consist of an organic cation, the most commonly used being dialkylimidazolium and tetraalkylammomiun salts, and a polyatomic inorganic anion (e.g. $\text{BF}_4{}^-$, $\text{PF}_6{}^-$) [9]. Due to their non-measurable vapour pressure, combined with the greater capillary force associated with their relatively high viscosity and the possibility of minimizing their solubility in the surrounding phases by the adequate selection of the cation and anion [2], it is possible to obtain very stable and environmentally friendly supported liquid membranes using ionic liquids as supported liquid phase.

Recently, we reported the selective simultaneous separation of the substrates and products of a transesterification reaction (vinyl butyrate, 1-butanol, butyl butyrate,

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doi:10.1016/j.memsci.2007.09.020

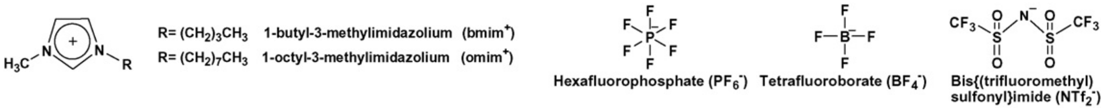

Fig. 1. Ions involved in the assayed ionic liquids.

and butyric acid) using SLMs based on two ionic liquids (ILs): 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim$^+$][PF$_6$$^-$], and 1-octyl-3-methylimidazolium hexafluorophosphate, [omim$^+$][PF$_6$$^-$] [12]. These SLM showed high operational and structural stability [12,13]. Significant differences in the selectivity values between both SLMs were observed, which led us to further investigate the effect of the nature of the ionic liquid used as liquid phase on the selectivity of the resulting SLM. In this work, six ionic liquids with different cation and anion compositions (see Fig. 1) were tested as liquid phase in SLMs for the separation of vinyl butyrate, 1-butanol, butyl butyrate, and butyric acid. The different cation and anion compositions of these ILs are reflected in their different hydrophilic/hydrophobic character [14,15], therefore, this parameter was also determined by the octanol–water partition coefficient (K_{ow}).

2. Experimental

2.1. Reagents and membranes

A polymeric membrane of 25 mm diameter from Millipore S.A. (Madrid, Spain) was used as supporting membrane, 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 hexafluorophosphate, [bmim$^+$][PF$_6$$^-$] (purity > 99%), 1-octyl-3-methylimidazolium hexafluorophosphate, [omim$^+$][PF$_6$$^-$] (purity > 99%), 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim$^+$][BF$_4$$^-$] (purity > 99%), 1-octyl-3-methylimidazolium tetrafluoroborate, [omim$^+$][BF$_4$$^-$] (purity > 99%) were purchased from Solvent Innovation GmbH (Cologne, Germany). 1-Butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, [bmim$^+$][TfN$_2$$^-$] (purity > 99%) was purchased from Sigma–Aldrich–Fluka Chemical Co. (Madrid, Spain) and 1-octyl-3-methylimidazolium bis{(trifluoromethyl) sulfonyl}imide, [omim$^+$][TfN$_2$$^-$] (purity > 99%) from Merck KgaA (Darmstadt, Germany). Substrates, solvents, and other chemicals were purchased from Sigma–Aldrich–Fluka Chemical Co. (Madrid, Spain), and were of the highest purity available.

2.2. Preparation of supported liquid membranes

Immobilization was conducted by placing the membrane in a 10 mL Amicon$^{\mathrm{TH}}$ ultrafiltration unit and adding 3 mL of ionic liquid. Nitrogen pressure at 2 bar was applied, and the ionic liquid flowed through the pores of the membrane. The pressure was released once a thin layer of ionic liquid was left on the upper surface of the membrane. This procedure was repeated three times to ensure that all the membrane pores were filled with liquid since the ionic liquids used are quite viscous. Then, the membrane was left to drip overnight to remove excess ionic liquid from the membrane surface.

2.3. Transport studies

The transport of vinyl butyrate, 1-butanol, butyl butyrate, and butyric acid through the SLMs was evaluated. The transport studies were performed at 30 °C using a glass diffusion cell with two independent compartments, with 30 mL each, separated by the SLM (Fig. 2). O-rings were inserted on each side of the SLM. The entire assembly was held together by a threaded connector.

In each experiment, the initial solute concentrations in the feed phase were 100 mM in *n*-hexane. *n*-Hexane was used as a receiving solution in all cases. The transport experiment was begun by adding 30 mL of each solution into their respective compartments. Both compartments were mechanically stirred to avoid concentration polarization conditions at the membrane interfaces. The solute concentrations were monitored by sampling 100 μL of each compartment at regular time intervals over 48 h. A hexane solution of ethyl hexanoate (internal standard) (100 μL, 60 mM) and *n*-hexane (800 μL) were added to the sampling vials and the resulting solution (1 mL) was analyzed by GC as described in Section 2.5.1.

Solute transport was analyzed by the permeability parameter ($\bar{P}$), which was calculated using Eq. (1) [12], from the slope of the plot of $\ln[(C_0 - 2C_{\mathrm{r}})/C_0]$ versus t

$$\ln\left[\frac{(C_0 - 2C_{\mathrm{r}})}{C_0}\right] = \frac{-2\bar{P}A}{V}t \qquad (1)$$

where C_0 is the initial solute concentration in the feed phase (mol L^{-1}), C_{r} the solute concentration in the receiving phase

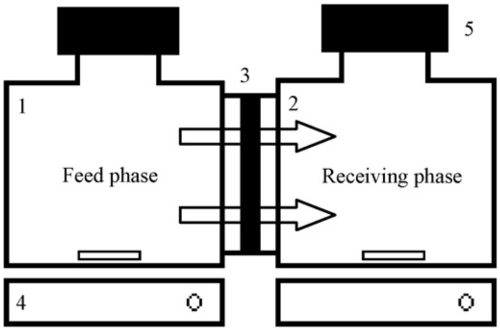

Fig. 2. Schematic illustration of the glass diffusion cell with two independent compartments used for transport experiments: (1) feed solution containing solutes; (2) receiving solution containing fresh solvent; (3) supported liquid membrane; (4) magnetic stirrer; (5) septum.