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Selective recovery of solutes from ionic liquids by pervaporation—a novel approach for purification and green processing

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Non-porous membranes with the selective layer consisting of hydrophilic or hydrophobic polymers have been applied for the quantitative and selective recovery of solutes with different physico-chemical properties from a room-temperature ionic liquid, ([bmim][PF_6]).

Room-temperature ionic liquids are fluids that consist entirely of organic cations and inorganic or organic anions and, as a consequence, they lack a measurable partial pressure.[1] This feature of ionic liquids permits their repeated use as benign solvents for green chemical syntheses without solvent loss to the environment due to evaporation.[2] The challenge for the equally benign recovery of solutes from ionic liquids remains and has been identified.[3] Conventional separation techniques for solute recovery either apply energy non-specifically to the bulk (distillation), or employ volatile organic solvents for extraction, thus cancelling out one of the ionic liquid's major advantages. 'Cleaner' and energy-efficient technologies for solute recovery from ionic liquids have recently been summarised to comprise supercritical carbon dioxide extraction and liquid–liquid extraction using aqueous systems or crown ether extractants.[4] Although supercritical carbon dioxide extraction is an efficient separation technique applicable to a wide range of separation problems, it remains technically demanding.[5] Here we demonstrate that pervaporation, as a highly selective and versatile membrane separation process, is capable of quantitatively recovering volatile solutes directly from ionic liquids, more effectively and under milder operating conditions than distillation. Choosing the appropriate membrane for the individual separation problem, pervaporation may prove more versatile than solvent extraction processes as well as more efficient and energetically more advantageous than evaporative techniques.

The separation principle of pervaporation is based on the preferential partitioning of a solute from a liquid feed phase into a dense, non-porous membrane through which it diffuses according to its chemical potential gradient.[6] This gradient is the driving force for the solute transport across the membrane. It is in general established by maintaining a low vacuum on the membrane downstream side, while keeping the membrane upstream side, which is in contact with the liquid feed, at ambient pressure. According to the solution-diffusion model, the partial flux J_i of a solute i across the membrane is given by eqn. (1):

$$J_i = \frac{S_i D_i}{z_m} \Delta\mu_i = \frac{S_i D_i}{z_m} (\mu_i^{\mathrm{f}} - \mu_i^{\mathrm{p}}) \qquad (1)$$

with S_i the partitioning coefficient of solute i between the feed liquid phase and the membrane; D_i the diffusion coefficient of i in the membrane; z_m the membrane thickness; $\Delta\mu_i$ the chemical potential gradient of i over the membrane; μ_i^{f} and μ_i^{p} are the chemical potential of i in the liquid feed phase and the permeate, respectively.

Any compound partitioning between the bulk solvent and the membrane can be recovered by pervaporation once there exists a chemical potential gradient over the membrane. For the same chemical potential gradient, pervaporation can be more effective than distillation for solute recovery.[7] The solute partitions from the bulk solvent into the membrane polymer where it sorbs. Due to the chemical potential gradient it then diffuses through the membrane polymer and subsequently desorbs on the membrane downstream side into the vacuum. This explains why pervaporation can also be applied to the recovery of low-volatile, high-boiling compounds at relatively moderate temperature: unlike distillation, pervaporation is not governed by the vapour–liquid equilibrium, but by solute–polymer interactions.[8] For an individual separation problem, it is therefore crucial to choose or develop the membrane polymer such that it exhibits a high selectivity for the target compounds under the separation process operating conditions. Otherwise, the process is not efficient.[9]

Energy consumption in pervaporation stems mainly from establishing the vacuum and condensing the solutes permeated. Specific to coupling pervaporation to ionic liquids is the fact that energy is spent very efficiently on the permeating solute only because no bulk solvent permeates the membrane. In contrast, during distillation energy is spent non-specifically on heating both the non-volatile bulk solvent and the solutes, with the latter often being present in minor concentrations.

Four case studies were chosen to test the promising concept of removing volatile solutes from ionic liquids by pervaporation: (1) water as a possible reaction product during, for example, condensations or esterifications, whose removal shifts the reaction equilibrium toward higher product yields; (2) ethyl hexanoate as a possible product of low volatility from a heat sensitive biotransformation; (3) chlorobutane as a possible residue stemming from the synthesis of the ionic liquid, whose removal increases significantly the purity of the latter; (4) naphthalene as a low-boiling compound.

Laboratory-scale pervaporation experiments were carried out using a range of binary solutions of the ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6], and model solutes all of which differ strongly in their physico-chemical properties. The ionic liquid was synthesised in our laboratory using a procedure reported.[10] The model solutes used were naphthalene, ethyl hexanoate, chlorobutane and water with initial feed concentrations of 15, 3.5, 20 and 17 kg m^{-3}, respectively. Different dense hydrophilic and hydrophobic polymeric membranes, namely poly(octylmethylsiloxane) (POMS) polyether block amide (PEBA) and poly(vinyl alcohol) (PVA) were chosen for the solute recovery based on their selectivity for the individual model solute. All experiments with results depicted in Figs. 1 and 2 were carried out at 323.15 K and a permeate pressure of 10 Pa, using a standard laboratory pervaporation set-up with an effective membrane area of 0.01 m^2.[11] The feed volume used was 110 cm^3 throughout all experiments. No ionic liquid was detected in any of the permeates, with the detection limit being 74 μg kg^{-1} using inductively coupled plasma (ICP) spectroscopy and phosphorus as the reference atom for the hexafluorophosphate anion of [bmim][PF_6]. Organic model solute concentrations in the feed and the permeate were determined by gas chromatography after extraction from the ionic liquid with diethyl ether. Water

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concentration in the ionic liquid was determined using an automated Karl–Fischer titrator.

Fig. 1 depicts the successful, quantitative recovery (> 99.2%) of all solutes tested by pervaporation. It should be noted that recovery rates apply for the small membrane area used in the laboratory and therefore appear uneconomically long. Because membrane area is relatively inexpensive, large-scale pervaporation units will employ larger membrane area/feed volume ratios, thus diminishing the time for quantitative solute recovery manifold, as can be simulated on the basis of the partial fluxes presented in Fig. 2.

Water exhibited the highest flux, using a hydrophilic PVA-composite membrane. Because of their hydrophilicity, PVA-membranes are highly permeable for water, while hindering the permeation of hydrophobic molecules.[12] This is particularly interesting for reversible condensation reactions or biocatalytic esterifications carried out in ionic liquids, during which the selective and continuous removal of the water formed shifts the equilibrium to higher yields of the target product.[12] The target product, such as esters formed by esterification, can then be recovered using an appropriate hydrophobic membrane, with an example being the pervaporation of ethyl hexanoate utilising a POMS-composite membrane (Figs. 1 and 2). It should be pointed out that especially with regard to biotransformations carried out in ionic liquids, pervaporation is the only separation technique that can be applied without either degrading the biocatalyst or interfering with the bioconversion: it can be efficiently operated at a moderate temperature, and does not require any extraction aid detrimental to the performance of the biocatalyst that, in turn, can be reused without loss of activity.[13]

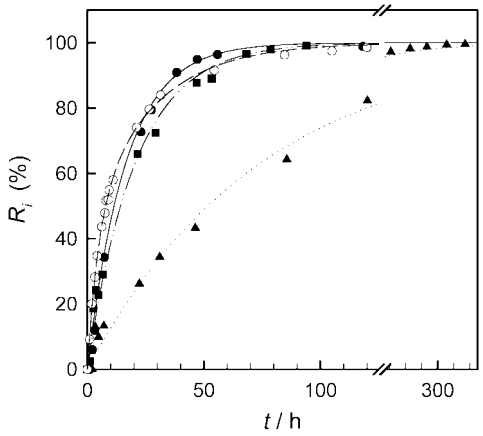

Fig. 1 Recovery of water by a PVA (4 μm)-composite membrane (○); chlorobutane (●) and ethyl hexanoate (■) by POMS (25 μm)-composite membrane; naphthalene by a homogeneous PEBA (30 μm)-membrane (▲). All solutes were recovered to a degree > 99.2% (limit of the analytical sensitivity) of their initial feed concentration.

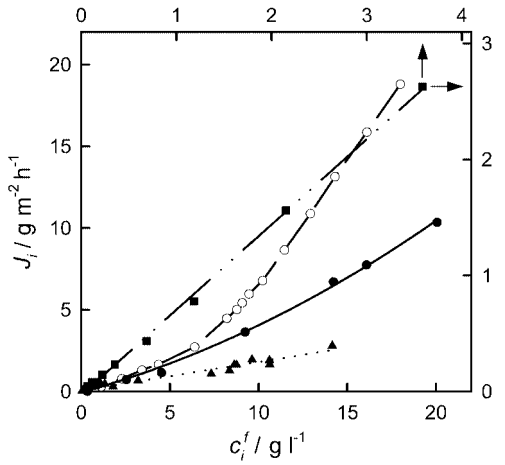

Fig. 2 Partial fluxes of the solutes recovered from [bmim][PF_6] as a function of their respective feed concentration. Experimental conditions and symbol legend are as reported in Fig. 1; for graphical reasons, the *x*- and *y*-axes for ethyl hexanoate are depicted on the top and on the right of the plot (indicated by arrows).

Once prepared, ionic liquids still contain solvent/reactant originating from their synthesis or the subsequent purification procedure. Commonly, these solvent residues are removed using evaporative techniques under high vacuum and/or an elevated temperature.[10] Utilising a POMS-composite membrane, chlorobutane as a solvent/reactant during synthesis of [bmim][PF_6] was recovered as depicted in Figs. 1 and 2, respectively. Pervaporation can hence be integrated in the production and purification process of ionic solvents for the recovery of volatile solvent residues, enabling a closed-loop production process for obtaining a pure ionic liquid at mild operating conditions.

The low-volatile model solute, naphthalene, was recovered quantitatively at 323 K, 168 K below its boiling point of 491 K (Figs. 1 and 2) using a homogenous PEBA-membrane. A homogenous membrane was chosen for this separation because in composite membranes the pressure loss in the porous support can be sufficient to cause undesired condensation of the low-volatile solute on the membrane downstream face. Although the rate of recovery was lower than that of the other solutes, owing to a smaller driving force, this example illustrates the potential pervaporation has for the recovery of high-boiling compounds.

In conclusion, pervaporation is a non-evaporative process that can be integrated in the production and purification process of ionic solvents for the selective recovery of volatile solvent residues at mild, and therefore energetically favourable, operating conditions. For the recovery of volatile solutes from heat sensitive reactions carried out in ionic liquids, such as bioconversions, pervaporation may be superior to other techniques.

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