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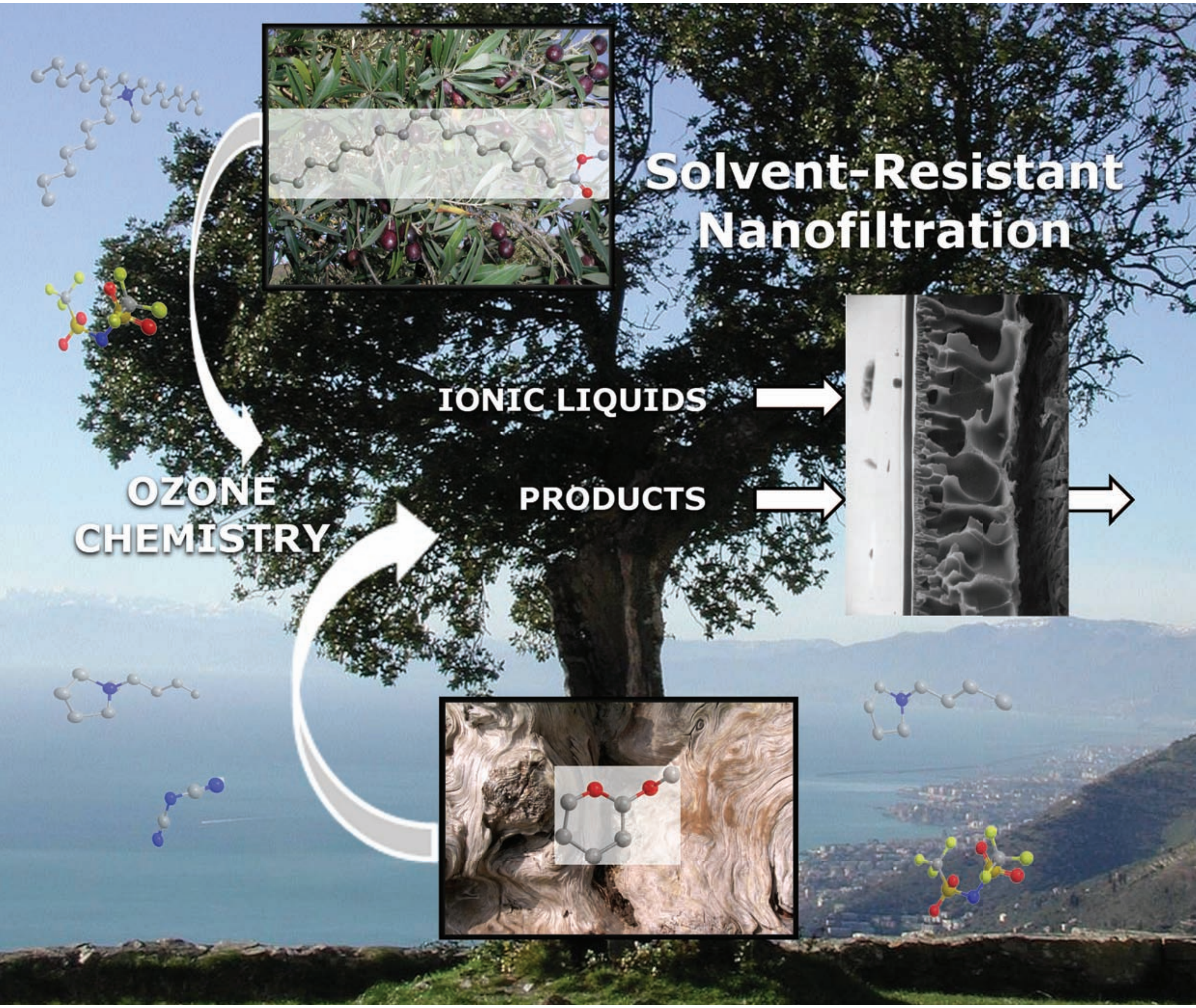

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Product recovery from ionic liquids by solvent-resistant nanofiltration: application to ozonation of acetals and methyl oleate

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In this work we tackle the problematic separation of reaction products from ionic liquid media. Solvent-resistant nanofiltration proves to be an attractive technique for the separation of non-volatile polar products from ionic liquids. In view of the high compatibility between ozone and ionic liquids, two ozone-mediated model reactions were chosen: firstly the oxidation of acetals to esters in the presence of ozone and secondly the ozonation of methyl oleate to monomethyl azelate and pelargonic acid. The objective was to retain the ionic liquid phase by means of a solvent-resistant nanofiltration membrane, while the organic reaction products permeate through the polymeric membrane. First, the ozonations were studied in order to know the characteristic product compositions. Next, a screening of membranes was performed on synthetic product mixtures. The second generation polyimide-based DuraMem™ membranes showed the highest rejection, up to 96%, for the evaluated ionic liquids. These DuraMem™ membranes also proved suitable for the separation of the products on real reaction mixtures, even in a single filtration step.

Introduction

Ionic liquids are a class of solvents consisting of large organic cations and smaller (in)organic counter ions. The ideal ionic liquids are liquid over a wide temperature range and exhibit a low vapour pressure. Ionic liquids are considered 'designer solvents': by a judicious choice of anion and cation the physicochemical properties of the ionic liquid can be adapted to the needs of a specific application. Ionic liquids have recently received wide attention as an environmentally benign alternative for volatile organic solvents.[1]

In a recent communication we demonstrated the high compatibility between ozone and ionic liquids.[2] Ozone can be produced *via* an electric discharge[3] and is a worthwhile choice for complex, multi-electron oxidations as only dioxygen is obtained as the by-product. However, the explosive nature of mixtures of ozone with the vapours of conventional organic solvents is a significant disadvantage.[4] Additionally, ozone is a detrimental agent in atmospheric aerosol formation, especially in the presence of organic compounds.[5] The introduction of ionic liquids can solve these issues as most ionic liquids have a close-to-zero vapour pressure at room temperature, thereby minimizing the explosion risk. Moreover, the formation of aerosols is suppressed, as the escape of liquid droplets or vapours from the solvent surface is impeded by the high viscosity, high surface tension and low vapour pressure of ionic liquids.

Despite these advantages offered by ionic liquids, efficient recycling of the ionic liquid and effective separation of the reaction products from the ionic liquid phase remain in several cases a challenge for industrial application. When the reaction products are apolar, judicious choice of the ionic liquid (IL) enables in specific cases their spontaneous expulsion from the ionic liquid, as we recently reported.[6] This offers an attractive alternative for the classical extraction with organic solvents. However, if the reaction products have a higher polarity, one has to revert to extraction with more polar solvents, in which the ionic liquid may partly or completely dissolve. This can potentially result in significant losses of ionic liquid in the product stream.[7]

Innovative unit operations like nanofiltration may show promise to overcome such separation issues.[7,8] The typical objective is to retain the charged ionic liquid by means of a membrane, while the organic reaction product permeates through the membrane. For this purpose, rather hydrophobic membranes with the appropriate *molecular weight cut-off* (MWCO) were selected. The recent introduction of chemically stable nanofiltration membranes may allow separation of non-volatile products from reaction media mainly consisting of ionic liquid. However, studies coupling *solvent resistant nanofiltration* (SRNF) with ionic liquid reactions are very rare.[7–10] For instance, the group of Livingston has addressed the issue, using the Suzuki cross-coupling as a model reaction.[7,10]

Therefore two ozone-mediated model reactions were chosen to study the product separation from ionic liquids applying SRNF: first the oxidation of acetals to esters in the presence of ozone, and second the ozonation of methyl oleate to monomethyl azelate and pelargonic acid. Acetals derived from aldehydes are known to react with ozone to yield ester type products.[11] Scheme 1 depicts the two possible pathways in the ozonation of 2-methoxytetrahydropyran (MTP): either lactone (δ-valerolactone, LA) formation or transformation to the open hydroxyester form (methyl 5-hydroxypentanoate, HE) which can be further oxidized to the carboxy ester 5-methoxy-5-oxovaleric

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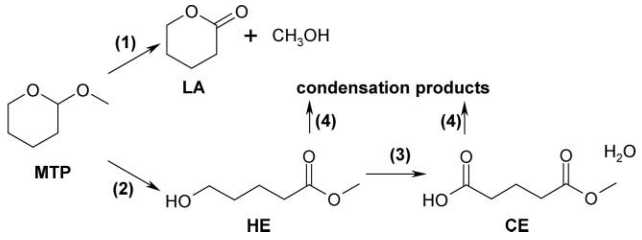


Scheme 1 Ozonation of 2-methoxytetrahydropyran (MTP), with formation of methyl 5-hydroxypentanoate (HE) or δ-valerolactone (LA). Methyl 5-hydroxypentanoate can be further oxidized to 5-methoxy-5-oxovaleric acid (CE).

acid (CE). We previously communicated that the pyrrolidinium-based ionic liquid [BMPyr][N(CN)$_2$] is an excellent reaction medium compared to the conventionally used organic solvents like acetic anhydride and ethyl acetate.[2] The ozonation proceeded not only faster but also more selectively in the ionic liquid.

The second reaction studied in this paper is the ozonolyis of methyl oleate. The industrial attention towards renewables, like methyl oleate, strongly increased as a result of the ever growing use and future depletion of fossil resources for both energy consumption and chemicals production.[12] Fatty acid esters present in seed oils are an alternative source of chemicals, since chemically they are closely related to the hydrocarbons in crude oil. Esters such as methyl oleate are normally derived from the transesterification of these seed oils with methanol, together with glycerol as a by-product.[13] Various transformations are possible with methyl oleate, since both the carboxylic group and the double bond can be modified. Possible C═C functionalizations include hydrogenation, hydroformylation, hydrosilylation, metathesis reactions, epoxidation and oxidative cleavage towards aldehydes, ketones or acids.[14] In particular, the oxidative cleavage of oleic acid or its methyl ester, leading to azelaic acid and pelargonic acid is interesting. Indeed, azelaic acid and its derivatives are applied in a broad range of industrial applications such as lubricants, plasticizers, adhesives, cosmetics and pharmaceuticals. The production of polymers like polyamides or polyesters represents another application area. Pelargonic acid is used as starting material for plasticizers and herbicides.[14] The industrial process uses ozone for the preparation of these acids.[15] In that process, the double bond, which is very reactive towards ozone, is first transformed into an ozonide, which can subsequently be split oxidatively to form the corresponding acids. Due to the high compatibility between ozone and ionic liquids and based on our experience with the acetal ozonations, it is also expected that in this case ionic liquids can contribute to a safer and greener transformation of methyl oleate, without aerosol formation.

In this work, we study these two model reactions in ionic liquids, with the primary focus on post-reaction product separation applying SRNF.

Results and discussion

Oxidation of acetals to esters in the presence of ozone

A prerequisite for applying ionic liquids in ozonolysis reactions is their chemical stability towards ozone. Before, we reported that pyrrolidinium-based ionic liquids are stable to ozone, while imidazolium-based ionic liquids proved sensitive to ozonolytic degradation, as demonstrated by NMR studies.[2] Pernak *et al.* also observed this fast degradation of imidazolium ionic liquids induced by ozone.[16] This was ascribed to the sensitivity of the C═C bonds to ozone. [BMPyr][N(CN)$_2$] with a melting point below −50 °C was shown to be a suitable solvent for the acetal oxidation. The ozonation proceeds not only faster but also more selectively in the ionic liquid:[2] in the ionic liquid only the HE and the over-oxidized CE were formed, which contrasts with the formation of the lactone product and condensation products (*e.g.* methyl 5-(4-methoxy-4-oxobutoxy)pentanoate) in the case of acetic anhydride as the solvent. Moreover, the traditional procedure requires acetic anhydride/sodium acetate for hydroxyl group trapping to inhibit over-oxidation to the corresponding carboxy ester.[11] From this reasoning, it is clear that ionic liquids are a more practical media for such ozone mediated transformations than the traditional low-boiling organic solvents.

However, considering the objective of product separation by means of SRNF, [BMPyr][N(CN)$_2$] is rather inappropriate in view of its low molecular weight (MW = 208.3 g mol^{-1}). A substantially higher molecular weight compared to the solutes' molecular weight often facilitates the solute separation from the ionic liquid phase.[17]

Screening of ionic liquids. Therefore various ionic liquids of higher molecular weight were assessed on their sensitivity towards ozone. Additional selection criteria were a low melting point and low viscosity. In a screening of 10 ionic liquids, only 1-butyl-1-pyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMPyr][Tf$_2$N], MW = 422.4 g mol^{-1}) and alkyldimethylbenzylammonium chloride (benzalkonium chloride, [BenzAlk][Cl]), with alkyl = C_8H_{17}–$C_{18}H_{37}$; MW = 283.5–423.5 g mol^{-1}) fulfilled these conditions.

These ionic liquids were tested as the reaction media in the ozonation of 2-methoxytetrahydropyran (MTP). Fig. 1 reports on the influence of the ionic liquid's nature on the hydroxy and carboxy ester yields. At 80 °C, MTP is totally converted towards the corresponding esters after only 1 h in the case of [BMPyr][Tf$_2$N]. The respective yields of hydroxy and carboxy ester were 55% and 45%. Note that the total ester yield after 1 h is 100%. Applying [BenzAlk][Cl] as the reaction medium, the reaction proceeded significantly more slowly, with a conversion

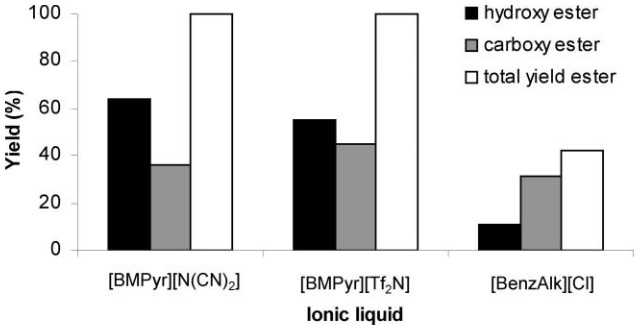


Fig. 1 Influence of choice of ionic liquid on the yield of hydroxy ester and carboxy ester (*Reaction conditions*: [*MTP*] = *5 mol L*$^{-1}$; *80 °C*; *1 h*; *0.21 mmol/min* O_3*-flow*).

of only 42% after a 1 h reaction time. The presumable reason for these observations is different ozone solubility. To the best of our knowledge, ozone solubility data in ionic liquids are at present not available. However, such data are available for oxygen. Anthony *et al.* evaluated the solubility of various gases in ionic liquids and stated that the oxygen solubility is generally rather low.[18] They also reported that pyrrolidinium ionic liquids and especially those containing the Tf_2N^- anion have slightly higher oxygen solubility values. It is plausible that the solubility variations of ozone follow similar trends. However, determining the ozone solubility in ionic liquids is not part of the scope of the present work but will be addressed in a forthcoming study which focuses on the detailed kinetics of ozone mediated reactions.

Next the effect of reaction temperature on the MTP ozonation in [BMPyr][Tf_2N] was investigated. Fig. 2 shows the evolution in HE and CE yields as a function of the reaction time at three different reaction temperatures. At 25 °C, the highest HE yield was attained after 4 h, with HE and CE yields of respectively 76% and 24%. Obviously, the reaction proceeded much faster at higher reaction temperatures. The maximum HE yield was reached after 2 h and 30 min at 50 °C (Y(HE) = 77%) and 80 °C (Y(HE) = 75%) respectively. It is striking that the same maximum HE yields are obtained at different reaction temperatures.

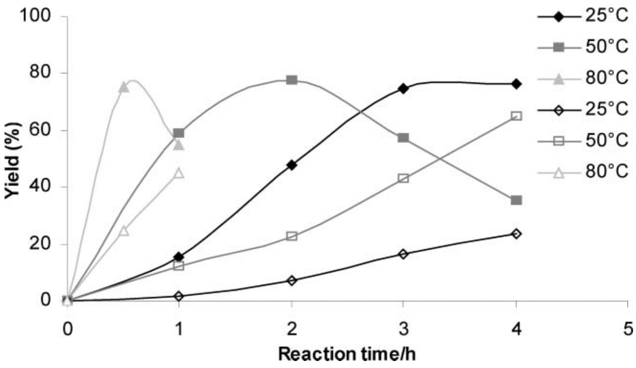


Fig. 2 Yield of hydroxy ester (filled symbols) and carboxy ester (open symbols) for the ozonation of MTP in [BMPyr][Tf_2N] (*Reaction conditions*: [*MTP*] = *5 M*; *0.21 mmol/min ozone flow*).

In conclusion, [BMPyr][Tf_2N], with a HE yield of 77% under mild conditions, is an excellent alternative for [BMPyr][$N(CN)_2$]. As the MW of the former ionic liquid is higher (422.4 g mol^{-1} *vs*. 208.3 g mol^{-1}), it is a more suitable candidate to be rejected by a SRNF membrane.

Post-reaction product separation by solvent resistant nanofiltration. There are two strategies for the separation of a product and the ionic liquid: either the product can be rejected while the ionic liquid permeates through the membrane (strategy I), or the IL can be rejected while the product permeates (strategy II).[9] In the acetal oxidation, the ionic liquids' molecular weight is higher than that of the products. Therefore strategy II will be used. Before subjecting the reaction mixtures to SRNF, a screening of polymeric membranes was performed. Therefore samples were prepared for filtration closely mimicking the reaction mixtures at 66% substrate conversion: 0.5 g of [BMPyr][Tf_2N], 1 mmol of MTP and 2 mmol of ethyl 3-OH-butyrate were dissolved in 2-butanone as solvent. Ethyl 3-OH-butyrate was chosen as an ester model compound, because of its functional group and molecular weight resemblance to the commercially unavailable methyl 5-hydroxypentanoate, the hydroxy ester derived from MTP. 2-Butanone was chosen as a solvent because it dissolves both the ionic liquid and the ester products. Note that water admixture was avoided to simplify the ensuing determination of the ionic liquid concentration in the filtrate phase by conductometry; the presence of water would require additional corrections. In a first step, the performance of a given membrane was assessed by its ionic liquid rejection (%). Because the MWCO of a membrane depends on the filtration conditions (like solvent, solute, transmembrane pressure and temperature)[19] the selection of a proper membrane for a given application often necessitates the screening of multiple membranes.[9] Recently, based on an earlier concept,[20] an adapted high-throughput filtration cell was designed in-house, which allows rapid membrane screening of very small feed volumes (see Experimental). The results of this membrane screening are presented in Table 1. For the best performing membranes (highest IL rejections) the permeabilities were also determined. Note that because of the small volumes collected in the membrane filtrations, the permeabilities are indicative, which explains the rather large standard deviations.

Table 1 Screening of membranes for rejection of the IL in test mixtures mimicking the acetal oxidation reaction mixtures[a][b]

Entry	Membrane	p (N_2)/bar	R_{IL} (%)[d]	Permeability (L m^{-2} h bar)
1	Zeol-PDMS/PAI1[c]	20	52 ± 3	—
2	Zeol-PDMS/PAI2[c]	20	87 ± 1	—
3	Zeol-PDMS/PI2[c]	20	90 ± 2	0.7 ± 0.3
4	Zeol-PDMS/PI3[c]	20	86 ± 4	—
5	STARMEM™ 122	40	52 ± 4	—
6	DuraMem™ 200	40	95 ± 2	0.15 ± 0.075
7[e]	DuraMem™ 200	40	91 ± 1	0.375 ± 0.05
8	DuraMem™ 200	20	54 ± 4	0.175 ± 0.025
9[f]	DuraMem™ 200	40	91 ± 1	0.45 ± 0.125
10	DuraMem™ 300	40	88 ± 1	0.5 ± 0.2

[a] Filtration conditions: 1000 RPM stirring, T = 20 °C. [b] Mixture: 0.5 g of [BMPyr][Tf_2N], 1 mmol of 2-methoxytetrahydropyran, 2 mmol of ethyl 3-OH-butyrate, 7 mL of 2-butanone. [c] Non-commercial asymmetric membrane coated with zeolite filled PDMS x times (x = 1, 2 or 3); PI = polyimide support layer; PAI = polyamidoimide support layer. [d] The indicated rejection ($R_{IL} = ((1 - C_P/C_F) \times 100\%)$ with C_P the concentration of the IL in the permeate and C_F the concentration of the IL in the feed) is an average of at least two filtrations. The standard deviation is also shown. [e] T = 50 °C. [f] Methanol was used as the solvent.

Because of the ionic character of the IL, rather hydrophobic membranes, with typically a low affinity for the IL compared to hydrophilic membranes, were screened. First, a range of PDMS-based membranes was prepared (Table 1, entries 1–4). Two different PI and PAI based supports were coated with zeolite ZSM-5 filled hydrophobic polydimethylsiloxane (PDMS) (see Experimental), with x in PIx (or PAIx) representing the number of PDMS coatings. Because PDMS is known to swell strongly in apolar solvents like toluene and ethyl acetate, the PDMS layer was filled with zeolites, which results in an increased cross-linking density by interaction of the zeolite silanol groups with the PDMS polymer chains.[21] We expect that 2-butanone, which has a polarity comparable to that of ethyl acetate, would induce a comparably strong swelling. The swelling of membranes causes an increase in the free space between the polymer chains, leading to lower solute rejections. By filling the PDMS layer with zeolites, if dispersed well, this swelling is strongly decreased, enhancing the solute rejection in these solvents.

It emerges from Table 1 that for the PAI supports, the rejection of the ionic liquid increased upon coating with additional PDMS layers. In the case of PAI, 2 coatings of PDMS gave a rejection of 87% at 20 bar of N_2 (entry 2), whereas one coating only led to a 52% rejection (entry 1). This could be expected since repeated coating with PDMS makes the top section more dense. Therefore the PI support was also coated with 2 coatings of PDMS. The PDMS based membranes on top of PI supports prove even more suitable for retaining the ionic liquid compared to those based on PAI supports: PI2 exhibited a rejection of 90% at 20 bar N_2 (entry 3) whereas PAI2 rejected 87% of the ionic liquid (entry 2). It appears that a coating with two PDMS layers is the optimum, as a further increase in the number of PDMS layers did not improve the performance of the membrane (entry 4). In addition, with increasing PDMS coatings, the thickness of the top layer increases, leading to lower membrane permeabilities. Summarizing, irrespective of the support used, both PDMS membranes retain the ionic liquid reasonably well from the test mixture.

In a next step, commercially available stable SRNF membranes with a low MWCO were investigated. As STARMEM™ 122 exhibited a very good performance in the rejection of trihexyl(tetradecyl)phosphonium chloride (MW = 519.31 g mol^{-1}) in a product mixture of a Suzuki coupling,[7] a preliminary filtration was performed with this membrane. However, this 'first generation' STARMEM membrane with a reported MWCO of 220 in toluene, led to a rejection of only 52% for [BMPyr][Tf_2N] (MW = 422.41 g mol^{-1}) in 2-butanone (Table 1, entry 5). Recently Membrane Extraction Technology Ltd developed 'second generation' SRNF membranes referred to as DuraMem™. These membranes were also tested on their applicability for rejecting ionic liquids. With DuraMem™ 200, the highest rejections for our application (95%, entry 7) were achieved. DuraMem™ 300 exhibited a lower rejection value of 88% (entry 10). Despite this lower rejection, the permeability through DuraMem™ 300 is higher (0.5 L m^{-2} h bar) compared to DuraMem™ 200 (0.15 L m^{-2} h bar).

Based on the good results with DuraMem™ 200, the effect of the filtration conditions was investigated. Increasing the filtration temperature to 50 °C resulted in a slight decrease in rejection, but the permeability was strongly enhanced (entry 7). With methanol as solvent, lower IL rejections (91%) but higher permeabilities (0.45 L m^{-2} h bar) were obtained (entry 9). This is possibly due to the higher affinity of the ionic liquid for methanol than for 2-butanone, leading to a better solvation of the ionic liquid. The smaller methanol solvent molecules drag the ionic liquid more effectively through the membrane, leading to lower rejections and higher permeabilities. Lowering the pressure to 20 bar of N_2 led to decreased IL rejections (54%, entry 8). A possible explanation is that upon applying higher pressure, the polymer chains in the membrane become more compact, resulting in higher rejections. Such lower rejections at lower pressure were observed before in literature[9] and are also consistent with the solution–diffusion theory as presented by Wijmans and Baker:[22] the driving force for the solvent is the pressure difference across the membrane. In contrast, solute transport is rather influenced by the concentration gradient. A higher pressure theoretically leads to a higher solvent permeation but the ionic liquid permeation remains more or less constant, resulting in a higher ionic liquid rejection.[23]

Table 2 Multi-step filtration with DuraMem 200™ of acetal oxidation reaction mixtures[a][b]

Filtration step	R_{IL} (%)[c]	Permeability (L m^{-2} h bar)
1	71 ± 2	0.175 ± 0.07
2	94 ± 2	0.275 ± 0.07
3	96 ± 3	0.425 ± 0.09

[a] Filtration conditions: p (N_2) = 40 bar, 1000 RPM stirring, T = 20 °C. [b] Reaction conditions: 2 g of [BMPyr][Tf_2N], 10 mmol of MTP, 80 °C, 0.21 mmol min^{-1} of ozone. [c] The indicated rejection $R = ((1 - C_P/C_O) \times 100\%)$ with C_P the concentration of the IL in the permeate and C_O the concentration of the IL in the original mixture, is an average of at least two filtrations. The standard deviation is also shown.

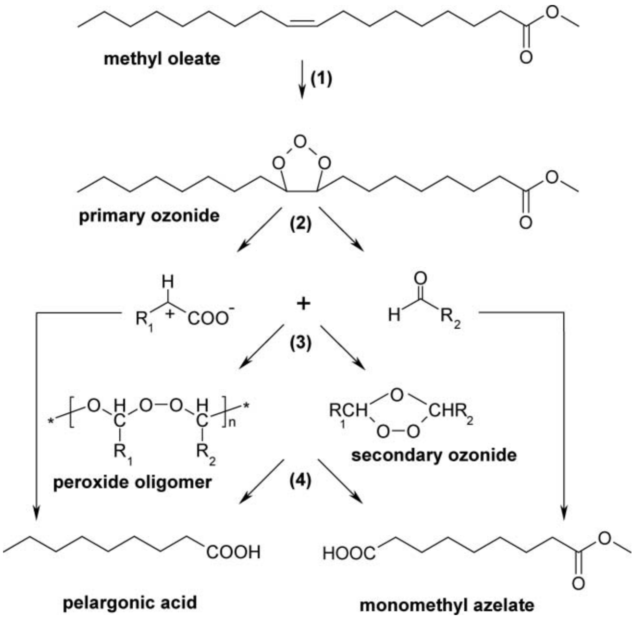
These results suggest that DuraMem™ 200 membranes can be used to recycle ionic liquids for the acetal oxidation. This was verified by applying these membranes in SRNF of real reaction mixtures. Hereto 10 mmol of 2-methoxytetrahydrofuran was ozonized (0.21 mmol min^{-1} ozone flow) in 2 g of [BMPyr][Tf_2N] at 80 °C. After reaction the mixture was diluted in 2-butanone (7 mL) and subjected to the SRNF. As can be seen in Table 2 the one step filtration of the reaction mixture resulted in only 71% of ionic liquid rejection. Therefore, after dilution with 2-butanone, the permeate was again filtered with the DuraMem™ 200 membrane: the ionic liquid rejection increased to 94%. A third filtration step even led to an ionic liquid rejection of 96%. Note that the permeability of the membrane was higher in the third step compared to the first step. This could be due to the decreased ionic liquid concentration in the reaction mixture, due to the dilution with 2-butanone.

Summarizing, DuraMem™ 200 was found to be an excellent membrane for the separation of the non-volatile hydroxy and carboxy ester from [BMPyr][Tf_2N] in the ozonation of acetals, with an ionic liquid rejection of 96%.

Ozonation of methyl oleate

The ozonation of methyl oleate (MO) is generally accepted to proceed *via* the Criegee mechanism: the electrophilic ozone molecule reacts with the C=C bond with formation of a primary ozonide (1,2,3-trioxolane) (step (1), Scheme 2).[24] This unstable primary ozonide splits into Criegee intermediates (peroxides) and aldehydes (step (2), Scheme 2).[25] These intermediates can recombine to form the secondary ozonide (step (3), Scheme 2). In a second phase, the secondary ozonides can be split oxidatively or thermally.[15,26] In the oxidative splitting, the secondary ozonide reacts with oxygen with formation of two carboxylic acids, pelargonic acid and monomethyl azelate. The optimal temperature for the latter reaction is just below 100 °C.[15] This reaction is traditionally performed in pure methyl oleate.

However, because of drawbacks such as evaporation losses and contamination of oxygen gas with organic vapors and organic particles, additional gas purification steps are required, at the expense of extra energy and effort.[15] By performing the ozonolysis reaction in ionic liquids, these extra steps can be avoided.



Scheme 2 Ozonolysis of methyl oleate *via* the Criegee mechanism (R_1 and R_2 are $–(CH_2)_7–COOMe$ and $–(CH_2)_7–CH_3$).

In a first step, a screening of ionic liquids was made based on good dissolution of methyl oleate, stability towards ozone and high MW for a good separation of the reaction products with SRNF. Out of the 15 tested ionic liquids, only methyltrioctylammonium bistriflimide ($[MOct_3N][Tf_2N]$, MW = 648.85 g mol^{-1}), methyltrioctylammonium trifluoroacetate ($[MOct_3][CF_3COO]$, MW = 481.73 g mol^{-1}) and trihexyltetradecylammonium dicyanamide ($[Hex_3TP][N(CN)_2]$, MW = 549,9 g mol^{-1}) exhibited the desired characteristics. $[MOct_3N][Tf_2N]$ was chosen as a model ionic liquid for the ozonation reaction, because of its high MW. The methyl oleate ozonation to pelargonic acid and monomethyl azelate is generally performed in two consecutive phases: an ozone phase, typically performed at lower temperatures, followed by a phase under pure oxygen.[15] With both the ozone and oxygen phase at 20 °C, the methyl oleate was fully converted in the ionic liquid to aldehydes and acids. As expected, there was a 50–50 ratio between the mono- (nonanal and pelargonic acid) and bifunctional products (methyl 9-oxononanoate and monomethyl azelate) (Table 3, entry 1). One can see from Table 3 that in the absence of water, increasing the reaction temperature of the oxygen phase from 20 °C to 100 °C did not influence the acid/aldehyde ratio of the monofunctional products much, with an acid/aldehyde ratio of 2.4 and 2.6 at 20 °C and 100 °C respectively (entries 1–2). In the case of the bifunctional products an increase to 7 was observed. Upon adding 10 wt% water and increasing the temperature during the oxygen phase to 100 °C, the yields of pelargonic acid and monomethyl azelate increased from 34 and 35 to 46 and 48% respectively (entries 3–4). It is well known that a reaction temperature around 100 °C is ideal for the oxygen phase in the ozonation of methyl oleate.[15] It seems that the higher temperature only promotes the aldehyde to acid oxidation if water is present. Water presumably functions as a proton carrier and source. Shortening the ozone phase and prolonging the oxygen phase (oxygen flow doubled) did not further improve the results (entry 5).

Table 3 Ozonation of MO in $[MOct_3N][Tf_2N]$ towards nonanal (**1**), pelargonic acid (**2**), methyl 9-oxononanoate (**3**) and methyl azelate (**4**)[a]

			Yield (%)			
Entry	Ozone phase[a]	Oxygen phase[a]	**1**	**2**	**3**	**4**
1	2 h/20 °C	5 h/20 °C	15	35	14	36
2	2 h/20 °C	5 h/100 °C	14	36	6	44
3[b]	2 h/20 °C	5 h/20 °C	16	34	15	35
4[b]	2 h/20 °C	5 h/100 °C	4	46	2	48
5[bc]	0.25 h/20 °C	7 h/100 °C	3	47	2	48

[a] 1 mmol methyl oleate, 1.5 g $[MOct_3][Tf_2N]$, phase 1 (ozone phase): 0.781 mmol O_3/min; stirring: 1000 RPM; phase 2 (oxygen phase): 0.25 L O_2/min; stirring: 500 RPM. [b] The mixture contained 10 wt% water with respect to the ionic liquid. [c] 0.50 L min^{-1} O_2.

In Fig. 3 the evolution of the product yields as a function of the reaction time is depicted. After the ozonation phase, the yield of the four ozonation products is around 25%. During the oxygen phase, the formed aldehydes are transformed towards the corresponding acids, with a summed acid yield of 94%, comprising both mono- and diacids, after 7 h.

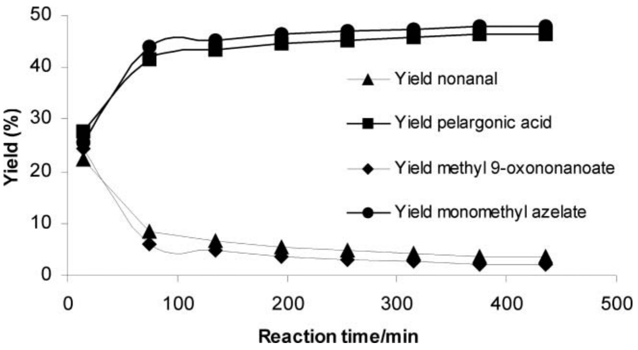


Fig. 3 Evolution of the product yields as a function of the reaction time (*reaction conditions*: 1 mmol methyl oleate, 1.5 g $[MOct_3][Tf_2N]$, *1) ozone phase: 0.25 h, 20 °C, 0.78 mmol* O_3*/min, 1000 rpm*; *2) oxygen phase: 7h, 100 °C, 0.50 L* O_2*/min, 500 rpm*).

Post-reaction product separation by solvent resistant nanofiltration. For the separation of the acid and ester products formed in the ozonolysis of methyl oleate, an analogous strategy was applied as for the acetals ozonation. Different membranes were tested, which are capable of retaining the larger IL while the smaller products permeate. For this preliminary screening samples to be filtered were prepared that simulate the reaction mixtures at 90% substrate conversion. 0.5 g $[MOct_3N][Tf_2N]$, 0.0333 mmol of methyl oleate, 0.3 mmol of azelaic acid and 0.3 mmol of pelargonic acid were dissolved in 2-butanone as solvent. 2-Butanone was chosen as a solvent as it solubilizes both the IL and the acid products. In this screening, a membrane was evaluated by its IL rejection (%) (Table 4).

As reported in Table 4, despite the higher MW of $[MOct_3N][Tf_2N]$ (MW = 648.85 g mol^{-1}) the first generation STARMEM™ membranes were again not capable of retaining the IL: STARMEM™ 120 rejected the IL for only 25% (entry 1), whereas STARMEM™ 122, which has a MWCO of 220 Da, showed a 40% rejection (entry 2). The rather non-selective STARMEM™ membranes still exhibited high fluxes: 413 and 275 L m^{-2} h for STARMEM™ 120 and STARMEM™ 122

Table 4 Screening of membranes for rejection of the IL in test mixtures mimicking the methyl oleate reaction mixtures[a b]

Entry	Membrane	R_{IL} (%)[c]	Permeability (L m^{-2} h bar)
1	STARMEM™ 120	25 ± 3	10.3 ± 3.0
2	STARMEM™ 122	40 ± 5	6.9 ± 5.7
3	DuraMem™ 200	81 ± 1	0.1 ± 0.025
4	DuraMem™ 300	96 ± 2	0.2 ± 0.1
5	DuraMem™ 300[d]	90 ± 0	0.375 ± 0.05
6	DuraMem™ 300[e]	93 ± 1	0.35 ± 0.1
7	DuraMem™ 300[f]	86 ± 5	0.5 ± 0.075

[a] Filtration conditions: p (N_2) = 40 bar, 1000 RPM stirring, T = 20 °C. [b] Mixture: 0.5 g of [$MOct_3N$][Tf_2N], 0.00333 mmol of methyl oleate, 0.3 mmol of azelaic acid, 0.3 mmol of pelargonic acid, 7 ml of 2-butanone. [c] Rejection R_{IL} : see Tables 1 and 2. [d] Filtration T = 50 °C. [e] Filtration pressure = 20 bar N_2. [f] Methanol as solvent.

respectively. A rejection of 40% is, however, too low for applying these SRNF membranes for the product recovery from the ionic liquid medium.

The DuraMem™ membranes exhibited a substantially better filtration performance. At 40 bar and with 2-butanone as solvent, DuraMem 200 and particularly DuraMem™ 300 led to higher IL rejections, with IL rejections of 81% and 96% respectively (entries 3–4). However, low membrane permeabilites were obtained. These low permeabilities could be improved to 0.375 L m^{-2} h bar by increasing the filtration temperature from 20 °C to 50 °C, however at the expense of an ionic liquid rejection decreasing from 96 to 90% (entry 5). Reducing the N_2 driving pressure to 20 bar also resulted in a lower IL filtration efficiency: whereas the ionic liquid rejection was slightly decreased, the membrane permeability was increased (entry 6). Replacing 2-butanone by methanol (entry 7) led to lower ionic liquid rejections (86%) but higher membrane permeabilities (0.5 L m^{-2} h bar), just as in the case of the acetal ozonation. This is remarkable since one would expect that a more polar solvent like methanol would cause less swelling of the membrane, thus leading to lower permeabilities and higher rejections. This indicates that the interactions between solvent, solute and membrane impart an important effect during the SRNF process.[21]

Again, the separation performances of the optimal membrane, DuraMem™ 300, were evaluated under the actual reaction conditions. The post-reaction mixture from the ozonation of methyl oleate (1 mmol of methyl oleate, 1.5 g of [$MOct_3$][Tf_2N], phase 1 : 0.5 h, 0.781 mmol min^{-1} O_3, 25 °C, phase 2 : 7 h, 0.250 L min^{-1} O_2, 100 °C) was diluted in 2-butanone, pressurized with 40 bar N_2 and filtered with DuraMem™ 300 (stirring: 1000 RPM; T = 20 °C). In contrast with the reaction mixture from the acetal ozonation, a one step filtration of the reaction mixture resulted in a 96% rejection of the IL with a permeability of 0.38 L m^{-2} h bar. The experiment was repeated five times, leading to a standard deviation of 2% and 0.05 L m^{-2} h bar for the rejection and the permeability respectively.

Conclusions

In summary, we proved that ionic liquids are excellent media for ozone mediated reactions, more specifically for the acetal oxidation and the ozonation of methyl oleate. The acetals are ozonized not only faster but also more selectively in ionic liquids compared to the traditional low-boiling organic solvents, with the only products being the hydroxy ester and the over-oxidized carboxy ester. Methyl oleate was oxidized in [$MOct_3N$][Tf_2N] towards pelargonic acid and monomethyl azelate, with a carboxylic acid yield of 94%. After selection of two suitable ionic liquids, 1-butyl-1-methylpyrrolidinium bistriflimide and methyltrioctylammonium bistriflimide, it was shown that solvent-resistant nanofiltration is an effective technique for separation of the ozonation products from the ionic liquid. Based on nanofiltration on synthetic product mixtures, it emerged that the highest permeability combined with a good IL rejection of 90% was achieved with the PI supported zeolite filled PDMS. However, the polyimide-based DuraMem™ membranes exhibited the highest rejections of ionic liquid (up to 96%). Moreover, these polymeric membranes proved highly efficient in separation of the products from real reaction mixtures. To our knowledge it is the first time that a SRNF membrane can separate reaction products efficiently from an ionic liquid like [BMPyr][Tf_2N] with a MW of only 422 g mol^{-1}. In only 3 steps the IL was rejected for 96%. For the higher MW ionic liquid [$MOct_3N$][Tf_2N], such rejections were even obtained after one single filtration step.

Experimental

Materials

Ionic liquids. Abbreviation list of ionic liquids: [$MOct_3N$][Tf_2N] (methyltrioctylammonium bistriflimide with bistriflimide = bis(trifluoromethylsulfonyl)imide); [BMPyr][$N(CN)_2$] (1-butyl-1-methylpyrrolidinium dicyanamide); [BMPyr][Tf_2N] (1-butyl-1-methylpyrrolidinium bistriflimide); [Benzalk][Cl] (alkyldimethylbenzylammonium chloride); [$MOct_3$][CF_3COO] (methyltrioctylammonium trifluoroacetate); [Hex_3TP][$N(CN)_2$] (trihexyltetradecylphosphonium dicyanamide). All [Tf_2N] and [$N(CN)_2$] based ionic liquids were obtained from Io-LiTec. [Benzalk][Cl] was purchased from Sigma Aldrich. [$MOct_3$][CF_3COO] was obtained from Merck. The water content of the ionic liquid batches used in the ozonation reactions and filtration experiments was less than 100 ppm for the hydrophobic ionic liquids and less than 1000 ppm for the halide containing ionic liquids. In non-halide ionic liquids, such as triflimides or dicyanamides, the halide content was typically less than 100 ppm.

Reagents. 2-Methoxytetrahydropyran, methyl oleate, 2-butanone, ester and acid reference compounds were obtained from commercial sources.

Membranes. Abbreviation list of membranes: Zeol-PDMS/PAIx (zeolite CBV 3002 filled PDMS coated polyamidoimide, with x indicating the number of PDMS coatings); Zeol-PDMS/PIx (zeolite CBV 3002 filled PDMS coated polyimide, with x indicating the number of PDMS coatings).

The STARMEM™ and DuraMem™ membranes, asymmetric SRNF membranes with an active layer of polyimide, in 'dry' form, were supplied by Membrane Extraction Technology

Table 5 Molecular weight cut off (MWCO) of commercial membranes[a]

Membrane	MWCO (Da)	Solvent[b]
STARMEM™ 120	200	toluene
STARMEM™ 122	220	toluene
DuraMem™ 150	150	acetone
DuraMem™ 200	200	acetone
DuraMem™ 300	300	acetone

[a] Obtained from Membrane Extraction Technology Ltd. [b] Solvent in which the MWCO is defined.

Ltd (UK) (www.membrane-extraction-technology.com). Their MWCO's are presented in Table 5.

Synthesis procedure of PDMS membranes

The zeolite filled polydimethylsiloxane (PDMS) coated polyimide (PI) membranes were synthesized according to the method described by Dobrak *et al.*[27] This membrane consists of a cross linked polyimide (Matrimid 5218) support layer, coated with zeolite (CBV 3002) filled PDMS. The PDMS layer is made from the pre-polymer RTV 615A and the cross-linker RTV 615B in a 10 : 1 ratio.

The zeolite filled PDMS coated polyamidoimide (PAI) membranes were prepared as follows. The support layer was prepared by casting a Torlon (Solvay) solution (18 wt% PAI, 61.5 wt% NMP and 20.5 wt% THF) on a polypropylene non-woven (FO 2471) kindly provided by Freudenberg (Germany). Therefore a custom-made casting knife, set at a gap of 250 μm, was used. After evaporation of the solvent (30 s), the resulting film was immersed in water (20 min) at room temperature. The prepared supports were afterwards subjected to a solvent-exchange procedure, involving immersion in isopropanol for three hours and subsequently for three days in a 40 : 40 : 20 (volume ratio) mixture of toluene/4-methyl-2-pentanone/mineral oil. Afterwards these films were wiped and dried at 60 °C for at least one hour. The first step in coating the support with PDMS is the preparation of the PDMS/filler suspension. Therefore 0.5 g of zeolite filler (CBV 3002 from PQ-corporation) was dispersed in hexane in an ultrasonic bath for one hour, followed by addition of 0.14 g of cross linker (RTV 615B). The mixture was stirred for two hours at 40 °C. Finally, 1.4 g of pre-polymer (RTV 615A) was added and the mixture was stirred for another hour at 60 °C (pre-polymerization). The PDMS/filler solutions were then coated on the PI support, which was taped onto a stainless steel plate, under an angle of 60°.[28] After evaporation of most of the solvent, this coating procedure was repeated with the membrane turned upside-down. The membrane was placed overnight at 110 °C to remove the rest of the solvent and to complete the cross linking.

Ozone stability test

Ozone resistance of ionic liquids can be evaluated by NMR, as well as macroscopically by investigating colour and viscosity changes. NMR spectroscopic measurements were carried out with a Bruker AMX-300 at 300 MHz (^{1}H) in deuterium oxide (D_2O) and 75.5 MHz (^{13}C) in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as standard. Additional NMR spectra were recorded on a Bruker Avance 400 spectrometer.

Typical procedure for acetal ozonation

The acetal (10 mmol) was dissolved in 2 g of ionic liquid and ozonized at 0–80 °C (rate of ozone supply: 0.21 mmol min^{-1}) for 8 h. Ozone was produced with a Fischer Ozone Generator type OZ 500. After reaction, the excess ozone was removed by flushing the system with nitrogen. Reaction mixtures in organic solvents were injected directly in the GC. The solutions in ionic liquids were first silylated with MSTFA (20 mol MSTFA/hydroxyl group; 80 °C; 2 h) and extracted with diethyl ether. The ether layer was analyzed with a Shimadzu 2014 GC equipped with a FID detector and an apolar CP-Sil 5 CB column. Note that after optimization of the filtration procedure, the extraction step was not needed anymore, because the IL could be simply retained with SRNF. The identity of the reaction products was verified by GC-MS. An Agilent 6890 gas chromatograph, equipped with a HP-5MS column, coupled to a 5973 MSD mass spectrometer was used.

Typical procedure for ozonolysis of methyl oleate

Typically 1 mmol of methyl oleate was dissolved in 1.5 g of $[MOct_3N][Tf_2N]$. First, the methyl oleate was ozonized at 20 °C (rate of ozone supply: 0.78 mmol min^{-1}) for 0.25–2 h. In a second phase, after flushing with nitrogen, oxygen was bubbled through the solution at 20–100 °C (rate of oxygen supply: 0.250 L min^{-1}) for 3.5–7 h. After reaction, the reaction mixture was transesterified overnight at 50 °C with 2% sulfuric acid in methanol (0.5 ml) and extracted with n-heptane. The heptane layer was analyzed analogously to the ether layer in the acetal oxidation. For the identification of the reaction products: see acetal oxidation.

Typical filtration procedure

Filtration experiments were performed on circular membranes (3.24 cm^2) using a stainless steel dead-end filtration cell in high throughput mode (10 × 10 ml) (Fig. 4). The ten filtration cells were filled with approximately 7 ml of the mixtures, stirred with a magnetic stirrer on a stainless steel filter plate positioned 7 mm above the membrane surface (1000 RPM) and pressurized with 20–40 bar of N_2. The filtrations were carried out at temperatures between 20–50 °C. The first ml of the filtrations was discarded (to avoid measuring under initial non-equilibrium conditions). For determination of rejections and fluxes the second and third ml were used. The ionic liquid rejection was calculated as

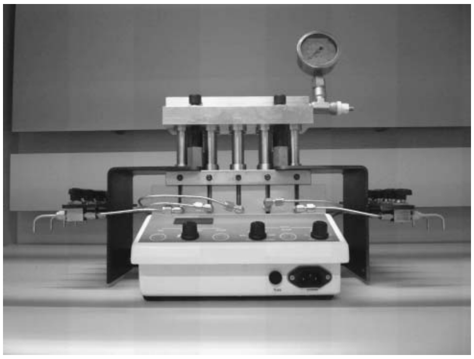


Fig. 4 High-throughput filtration cell (10 × 10 ml) designed in-house.

$R_{IL} = ((1 - C_P/C_F) \times 100\%)$ with C_P the concentration of the ionic liquid in the permeate and C_F the concentration of the ionic liquid in the feed. The ionic liquid concentration in feed and permeate was measured using conductometry using a Consort K 620 laboratory conductometer with Pt electrode. Firstly, a calibration curve which indicates the ionic liquid concentration as a function of the measured current was made based on mixtures with known ionic liquid concentrations. Based on this curve, the ionic liquid concentration in the permeates was determined.

In the multi-step filtration experiments, the permeate was collected from just after the pressurisation until 4 ml of the feed (9 mL) had permeated. The same high throughput filtration cell and conditions were used as in the single step filtration. After filtration, the filtration cell was depressurized and approximately 4 ml of 2-butanone was added to the permeate, to reach again the initial feed volume (9 ml). This new feed was then subjected to a next filtration step. In total, three filtration steps were performed.

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