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## Physical Chemistry of Ionic Liquids

### Guest Editor: Frank Endres (Technical University of Clausthal, Germany)

# Spontaneous product segregation from reactions in ionic liquids: application in Pd-catalyzed aliphatic alcohol oxidation†

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A methodology is introduced to separate polar reaction products from ionic liquids without the need for organic solvent extraction or distillation. We investigated product isolation after an alcohol oxidation performed in ionic liquids. Suitable ionic liquids were selected based on their mixing or demixing with a range of alcohols and the derived ketones. The aim was to obtain complete miscibility with the alcohol substrate at reaction temperature and a clear phase separation of the derived ketone product at room temperature. Six imidazolium based ionic liquids displayed this desired behaviour and were sufficiently stable to oxidation. These ionic liquids were then employed in the oxidation of non-activated aliphatic alcohols with molecular oxygen in the presence of palladium(II) acetate. In 1-butyl-3-methylimidazolium tetrafluoroborate, 2-ketone yields of 79 and 86% were obtained for, respectively, 2-octanol and 2-decanol. After cooling to room temperature the ionic liquid expels the immiscible ketone and the product phase can be isolated by decantation. In addition, the ionic liquid acts as an immobilization medium for the palladium catalyst, allowing efficient catalyst recycling.

## Introduction

The selective oxidation of alcohols is an important transformation in chemical industries owing to the abundant use of the derived carbonyl compounds as intermediates in the production of fine chemicals and pharmaceuticals. Numerous oxidizing agents are available for this key reaction.[1–3] Unfortunately, these reagents are generally consumed stoichiometrically and they often have a toxic nature, which demands costly purification processes to obtain non-noxious end products.[4–7] In view of the ever-growing environmental concern, more sustainable processes, e.g. productive catalytic transformations with safe reagents, became a principal R&D focus in all chemical industries. Therefore, the development of selective oxidation processes that use environmentally benign oxidants represents a significant challenge. The palladium catalyzed oxidation with molecular oxygen is truly a worthy alternative for traditional processes with metal oxides and metal salts.[5,7] Moreover, molecular oxygen is a relatively cheap oxidant and only water is formed as a by-product (Scheme 1).[8]

In 1998, Peterson and Larock reported the palladium catalyzed oxidation of alcohols in DMSO with $O_2$.[9] Given the favourable oxidation potential in DMSO for the reoxidation of palladium, an extra co-oxidant such as $CuCl_2$ proved unnecessary. Although this system shows several advantages, important drawbacks, related to the specific nature of DMSO, remain. DMSO is toxic and difficult to fully separate from the product, leading to a problematic recycling of the catalyst and solvent. These problems could be overcome by applying ILs, of which the polarity is comparable with DMSO.

Ionic liquids (ILs) receive increasing interest as green alternatives for the conventional volatile organic media owing to their unique solvent properties.[10–14] Recently, numerous transition metal catalyzed systems in ILs for alcohol oxidations were introduced.[15–21] In some cases the IL even served as solvent and catalyst, e.g. with a catalytic metal species part of the IL's anion.[22–24] While such catalytic systems performed well for allylic or benzylic alcohols, they were not very active for non-activated aliphatic alcohols. Moreover, the inevitable need for an extraction step to separate the reagent/product from the IL phase makes this approach less attractive.

We previously reported on a recyclable IL, based on the spontaneous expulsion of the product from the IL, for the catalytic hydrogenolysis of aromatic ketones.[25] In line with our previous work, we now present a catalytic IL system for the alcohol oxidation which allows ketone product isolation, without an extracting solvent. Applying the concept of temperature dependent miscibility of ILs and organic components, a selection of ILs was made which formed one homogeneous phase with the substrate at reaction temperature, while after cooling to room temperature, phase separation occurs. This enables product isolation by simple decantation.

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**Scheme 1** The palladium catalyzed oxidation of secondary alcohols using molecular oxygen.

In the class of alcohols, aliphatic alkanols were selected as substrates, as they are non-activated and not easily oxidized to ketones in good yields. Furthermore, the IL acts as an immobilization medium for the catalyst, which leads to an efficient catalyst recycling.

## Experimental

### Materials

Abbreviaton list of ILs: [MOct$_3$N][Tf$_2$N] (methyltrioctyl-ammonium bistriflimide with bistriflimide = bis(trifluoromethyl-sulfonyl)imide); [MOct$_3$N][CF$_3$CO$_2$] (methyltrioctylammonium trifluoroacetate); [H$_3$TP][N(CN)$_2$] (trihexyltetradecyl-phosphonium dicyanamide); [MIM][HSO$_4$] (1-methylimidazo-lium hydrogensulfate); [CNMMIM][Tf$_2$N] (1-methylnitrile-3-methyl-imidazolium bistriflimide); [EMIM][BF$_4$] (1-ethyl-3-methylimidazolium tetrafluoroborate); [EMIM][Tf$_2$N] (1-ethyl-3-methylimidazolium bistriflimide); [EMIM][CH$_3$CO$_2$] (1-ethyl-3-methylimidazolium acetate); [EMIM][CF$_3$CO$_2$] (1-ethyl-3-methylimidazolium trifluoroacetate); [EMIM]-[EtSO$_4$] (1-ethyl-3-methylimidazolium ethylsulfate); [EMIM]-[MeSO$_3$] (1-ethyl-3-methylimidazolium methanesulfonate); [EMIM][TsO] (1-ethyl-3-methylimidazolium tosylate); [BMIM][BF$_4$] (1-butyl-3-methylimidazolium tetrafluoroborate); [BMIM][Tf$_2$N] (1-butyl-3-methylimidazolium bistriflimide); [BMIM][TfO] (1-butyl-3-methylimidazolium triflate); [BMIM][Cl] (1-butyl-3-methylimidazolium chloride); [BMMIM][BF$_4$] (1-butyl-2,3-dimethylimidazolium tetrafluoroborate); [BMMIM][Tf$_2$N] (1-butyl-2,3-dimethyl-imidazolium bistriflimide); [BMMIM]-[CH$_3$CO$_2$] (1-butyl-2,3-dimethylimidazolium acetate); [DMIm]-[TfO] (1-decyl-3-methylimidazolium triflate); [BMPyr][CF$_3$CO$_2$] (1-butyl-1-methylpyrrolidinium trifluoroacetate); [BMPyr][N(CN)$_2$] (1-butyl-1-methylpyrrolidinium dicyanamide); [BMPyr][Tf$_2$N] (1-butyl-1-methylpyrrolidinium bistriflimide); [CNBMPyr]-[Tf$_2$N] (1-butylnitrile-1-methylpyrrolidinium bistriflimide); [CNEMPyr] [Tf$_2$N] (1-ethylnitrile-1-methylpyrrolidinium bis-triflimide); [Chol][Tf$_2$N] (choline bistriflimide); [Chol][CH$_3$CO$_2$] (choline acetate); [Chol][Ace] (choline acesulfamate); [Hbet]-[Tf$_2$N] (betainium bistriflimide).

The Pd(OAc)$_2$ catalyst and all alcohol reagents and ketone reference compounds were obtained from commercial sources. All imidazolium-based ILs except for [EMIM][Tf$_2$N], [BMIM][Tf$_2$N], [BMMIM][CH$_3$CO$_2$], [BMMIM][Tf$_2$N] and [CNMMIM][Tf$_2$N] were obtained from IoLiTec or Merck. [MOct$_3$N][Tf$_2$N], [H$_3$TP][N(CN)$_2$], [BMPyr][CF$_3$CO$_2$], [BMPyr][N(CN)$_2$] and [BMPyr][Tf$_2$N] were purchased from IoLiTec. The other ILs were synthesized in our laboratories based on synthesis procedures reported in literature.[26–28] The water content of the ionic liquid batches used in the oxidation reactions was less than 100 ppm for the hydrophobic ILs and less than 1000 ppm for the halide containing ionic liquids. In non-halide ILs, such as bistriflimides or acetates, the halide content was typically less than 100 ppm.

### Miscibility tests

The miscibility of reagents and reaction products with ILs was evaluated by a simple visual test under optical magnification. Mixtures were prepared to simulate two reaction mixture compositions representative of two specific stages (0 and 70% substrate conversion) in the course of the oxidation reaction. In order to mimic the initial reaction conditions, a 100 mol% alcohol/0 mol% ketone mixture ('100/0') was prepared consisting of alcohol (5 mmol) and IL. The mass ratio IL/alcohol was 1/1. The conditions at 70% conversion were simulated with a 30 mol% alcohol/70 mol% ketone mixture ('30/70') containing alcohol (1.5 mmol), ketone (3.5 mmol), water (3.5 mmol) and the same amount of IL as used in the '100/0' mixture. The mixtures were introduced in a viewing cell and were heated at the reaction temperature (90 °C) for 4 h while stirring (1000 rpm). The mixing behaviour of the different alcohol/(ketone, water)/IL combinations at the reaction temperature was evaluated visually. Afterwards, the mixtures were cooled to room temperature, allowed to stand overnight, and the mixing behaviour was re-evaluated.

### Oxidation experiments

Oxidation reactions were performed in stainless steel auto-claves (10 mL) under O$_2$ atmosphere (10–30 bar) at 90–140 °C for 2–24 h. The reaction mixtures were stirred magnetically (1000 rpm) and the reaction temperature was controlled with a thermocouple. A manometer was used to monitor the pressure changes during the reaction. A typical starting mixture consisted of the alcohol (10 mmol), the same mass of ionic liquid and 1 mol% Pd(OAc)$_2$ with respect to the alcohol. After reaction, the mixtures were allowed to cool down to room temperature. The upper layer was analyzed with a Shimadzu 2014 GC equipped with an apolar CP-Sil 5 CB column and a FID detector. The identity of the reaction products was verified by reference compounds and GC-MS. An Agilent 6890 gas chromatograph, equipped with a HP-5MS column, coupled to a 5973 MSD mass spectrometer was used.

### NMR spectroscopic measurements

NMR Measurements were carried out with a Bruker AMX-300 at 300 MHz ($^1$H) in deuterium oxide (D$_2$O).

## Results and discussion

### Miscibility of ionic liquids with alcohols and ketones

When performing oxidation reactions in ILs, it is required that: (1) the IL has a melting point lower than the reaction temperature; (2) the IL is chemically stable towards oxygen; (3) in order to simplify the product separation after the oxidation reaction, the IL should be miscible with the alcoholic substrates at a typical reaction temperature (e.g. 90–120 °C) and immiscible with the ketone products at room temperature. The strong resemblance between the polarity of the reagent and the product makes the selection of an IL with the desired phase behaviour difficult. In a previously published paper it was already found that the simplest reaction type to obtain the desired phase behaviour is one in which a more polar reagent is transformed into a more apolar product.[25] Indeed, ILs will more readily dissolve more polar compounds. The ideal ILs thus lead to one homogeneous reaction phase at the reaction temperature and phase separation at room temperature enabling simple product isolation by decantation (Scheme 2).
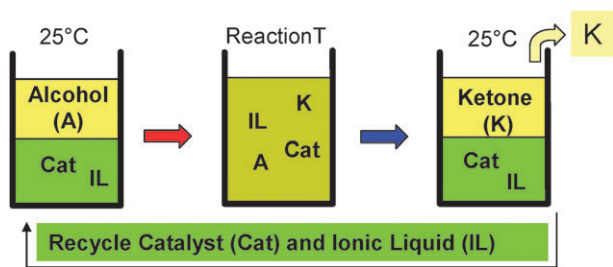
**Scheme 2** Recyclable catalytic ionic liquid system using the concept of temperature dependent miscibility of ionic liquids and organic components.

To mimic the initial conditions, 100 mol% alcohol/0 mol% ketone mixtures ('100/0') were prepared in various ILs. The reaction mixture composition at 70% conversion was simulated with a 30 mol% alcohol/70 mol% ketone mixture ('30/70'), adding extra water in an amount equimolar to that of the ketone used. Water was added to closely resemble the actual reaction conditions, since water is generated stoichiometrically (Scheme 1). For this screening phase, 2-octanol and 1-phenylethanol were selected as model substrates for aliphatic and aromatic alcohols respectively. Mixtures that appeared as a single, clear phase without any visible interface or cloudiness were considered as miscible ('1' in Tables 1 and 2). Other ILs proved immiscible with the alcohol or ketone compounds, resulting in a distinct interface between the two phases ('2' in Tables 1 and 2). The results of these miscibility tests are summarized in Table 1 (abbreviations of the ILs are given in the Experimental section). Suitable ILs form a homogeneous phase with the alcohol at reaction temperature ('1' in 100/0 column) but exhibit phase separation with the ketone ('2' in 30/70 column) upon cooling to room temperature. It should be noted that ILs containing the [PF$_6$] anion were not assessed because of their pronounced sensitivity to hydrolysis.

Firstly, the results for 2-octanol will be discussed. As shown in Table 1, the ammonium-based ILs of the [MOct$_3$N][X] type did not display the desired mixing behaviour, since no phase separation was observed for the 30/70 mixtures after cooling to room temperature (Table 1, entries 1 and 2). Presumably, van der Waals interactions between the ILs' octyl chains and 2-octanone enhance the miscibility of the IL with the ketone.[29] Similar behaviour was observed for other classes of ILs bearing longer alkyl chains: both trihexyltetradecyl-phosphonium dicyanamide ([H$_3$TP][(CN)$_2$N]) (entry 3) and 1-decyl-3-methyl-imidazolium triflate ([DMIM][TfO]) (entry 4) remained miscible with the ketone at room temperature which can also be ascribed to van der Waals interactions. In the case of [H$_3$TP][(CN)$_2$N], where the 100/0 mixture formed one clear phase, the 30/70 mixture did not, which can be explained with the presence of water in the 30/70 mixture. The fact that a mixture 100/0 turned from clear to cloudy upon water addition corroborates this hypothesis. This could be expected as the long alkyl chains make this IL behave like an aliphatic hydrocarbon, with poor affinity for water.

Next, imidazolium-based ILs functionalized with short alkyl chains were assessed (entries 4–19). The Brønsted acid [MIM][HSO$_4$] IL proved immiscible with 2-octanol at reaction temperature (entry 5). Introducing a nitrile group into the

cation, as in [CNMMIM][Tf$_2$N], did not result in sufficient miscibility with the model substrate either (entry 6). This IL would have been highly valuable in view of the stabilizing effect of the coordinating nitrile group on metal ions or colloids.[30] On the other hand, several 1-ethyl-3-methylimidazolium ([EMIM]) ILs led to the appropriate mixing behaviour in the case of 2-octanol/2-octanone (entries 7–13), except for cases like 1-ethyl-3-methyl imidazolium tetrafluoroborate ([EMIM][BF$_4$]) (entry 7) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf$_2$N]; entry 8). Most probably, the combination of a rather short alkyl chain on the cation and a more hydrophobic anion like [BF$_4$] or [Tf$_2$N] in the IL enhances its miscibility with both 2-octanol and 2-octanone and hence no phase separation was observed upon cooling of the 30/70 mixture to room temperature. However, the combination of a short alkyl chain cation with a more polar anion substantially decreased the IL's miscibility with 2-octanone at room temperature without affecting the solubility of the alcohol at reaction temperature. This is evidenced in Table 1 where EMIM combined with the more polar anions acetate ([MeCO$_2$]), ethyl sulfate ([EtSO$_4$]), tosylate ([TsO] or methane sulfonate [MeSO$_3$] (entries 9, 11-13) exhibited the desired phase behaviour: mixing with the 2-octanol on reaction temperature but phase separating with the 2-ketone product at room temperature. Unexpectedly, after replacing the acetate anion with trifluoroacetate (entry 10), the IL remained miscible with the ketone, pointing to the complexity of the IL selection.

The mixing behaviour of the 1-butyl-3-methylimidazolium ([BMIM]) solvent series was slightly different as compared to that of the EMIM based ILs (entries 14–17), and comparing both series also allows to draw some conclusions on the role of the anion. While the behaviour of [Tf$_2$N] based ILs seems independent of the cation (entries 8, 15, 19 and 23), this was not the case for ILs containing the tetrafluoroborate anion. Both [EMIM][Tf$_2$N] and [BMIM][Tf$_2$N] proved miscible with 2-octanone (entries 8, 15). 1-Butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF$_4$], in contrast with [BMIM][Tf$_2$N] and [BMIM][TfO], exhibited phase separation with the ketone upon cooling to room temperature (entries 14–16). The same phase behaviour was observed for 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) (entry 17). Note that at 90 °C, the mixture with [BMIM][BF$_4$] did not form one homogenous phase. Nevertheless, the volume of the IL phase strongly increased due to dissolution of the alcohol substrate. Note that upon further increasing to 120 °C the miscibility enhanced and nearly one phase was formed. It is assumed that sufficient contact between the substrate and the catalyst in the IL will be established to perform the catalytic oxidation. Interestingly, introducing a methyl group on the C-2 position of the imidazolium ring of the IL, e.g. in 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [BMMIM][BF$_4$], decreased the miscibility of 2-octanol and 2-octanone with the IL dramatically (entry 18). However in combination with other anions, like acetate and [Tf$_2$N], the [BMMIM] based ILs were completely miscible with both alcohol and ketone (entries 19–20).

Next, 1-butyl-1-methylpyrrolidinium ([BMPyr]) based ILs were tested (entries 21–23). Irrespective of the anion, the pyrrolidinium ILs proved not suitable. Although they formed

**Table 1** Miscibility of ammonium, phosphonium, imidazolium, pyrrolidinium, and choline- and betainium-based ionic liquids with 2-octanol/2-octanone and 1-phenylethanol/acetophenone mixtures[a,b]

| Entry | Ionic liquid | 2-Octanol 2-octanone | | 1-Phenyl ethanol acetophenone | |
|---|---|---|---|---|---|
| | | 100/0 | 30/70 | 100/0 | 30/70 |
| 1 | [MOct$_3$N][Tf$_2$N] | 1 | 1 | 1 | 1 |
| 2 | [MOct$_3$N][CF$_3$CO$_2$] | 1 | 1 | —[e] | —[e] |
| 3 | [H$_3$TP][(CN)$_2$N] | 1 | 1[c] | —[e] | —[e] |
| 4 | [DMIM][TfO] | 1 | 1 | 1 | 1 |
| 5 | [MIM][HSO$_4$] | 2 | 2 | 2 | 2 |
| 6 | [CNMMIM][Tf$_2$N] | 2 | 1 | —[e] | —[e] |
| 7 | [EMIM][BF$_4$] | 2 | 2 | 2 | 1 |
| 8 | [EMIM][Tf$_2$N] | 1 | 1 | 1 | 1 |
| 9 | [EMIM][CH$_3$CO$_2$] | 1 | 2 | 1 | 1 |
| 10 | [EMIM][CF$_3$CO$_2$] | 1 | 1 | 1 | 1 |
| 11 | [EMIM][EtSO$_4$] | 1 | 2 | 1 | 1 |
| 12 | [EMIM][TsO] | 1 | 2 | 1 | 1 |
| 13 | [EMIM][MeSO$_3$] | 1 | 2 | 1 | 1 |
| 14 | [BMIM][BF$_4$] | 1[d] | 2 | 1 | 2 |
| 15 | [BMIM][Tf$_2$N] | 1 | 1 | 1 | 2 |
| 16 | [BMIM][TfO] | 1 | 1 | 2[f] | 1 |
| 17 | [BMIM][Cl] | 1 | 2 | —[e] | —[e] |
| 18 | [BMMIM][BF$_4$] | 2 | 2 | 1 | 1 |
| 19 | [BMMIM][Tf$_2$N] | 1 | 1 | 1 | 1 |
| 20 | [BMMIM][CH$_3$CO$_2$] | 1 | 1 | —[e] | —[e] |
| 21 | [BMPyr][CF$_3$CO$_2$] | 1 | 1 | 1 | 1 |
| 22 | [BMPyr][(CN)$_2$N] | 1 | 1 | 1 | 1 |
| 23 | [BMPyr][Tf$_2$N] | 1 | 1 | —[e] | —[e] |
| 24 | [CNBMPyr][Tf$_2$N] | 2 | —[e] | —[e] | —[e] |
| 25 | [CNEMPyr][Tf$_2$N] | 2 | —[e] | —[e] | —[e] |
| 26 | [Hbet][Tf$_2$N] | 1 | 1 | 2[f] | 1 |
| 27 | [Chol][Tf$_2$N] | 1 | 1 | 1 | 1 |
| 28 | [Chol][CH$_3$CO$_2$] | 1 | 2 | —[e] | —[e] |
| 29 | [Chol][Ace] | 2 | 2 | —[e] | —[e] |

[a] Conditions: 100/0 mixture: alcohol (5 mmol), ionic liquid, mass ratio IL/ketone = 1/1, 120 °C; 30/70 mixture: 1.5 mmol alcohol (1.5 mmol), ketone (3.5 mmol), water (3.5 mmol), ionic liquid, same amount of IL as for 100/0 mixture, 20 °C. [b] '1': Mixtures that appeared as a single, clear phase without any visible interface or cloudiness; '2': Mixtures that exhibited a distinct interface between the two separated phases. [c] Upon cooling to room temperature, the mixture appeared as one but cloudy phase, probably due to the water present. [d] At reaction temperature the volume of the ionic liquid phase is increased by > 50% due to dissolution of the alcohol in the ionic liquid. [e] '—': solubility experiment not performed. [f] Mixture consists of 2 phases, but the volume of the ionic liquid phase is slightly (∼10%) increased due to dissolution of alcohol.

**Table 2** Miscibility of selected imidazolium IL with a series of different alcohol/ketone mixtures[a,b]

| Entry | Ionic liquid | 2-Butanol 2-butanone | | 2-Hexanol 2-hexanone | | 2-Decanol 2-decanone | | 2-Dodecanol 2-dodecanone | | 1-Octanol 1-octanal | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 100/0 | 30/70 | 100/0 | 30/70 | 100/0 | 30/70 | 100/0 | 30/70 | 100/0 | 30/70 |
| 1 | [EMIM][CH$_3$CO$_2$] | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 1 |
| 2 | [EMIM][EtSO$_4$] | 1 | 1 | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 |
| 3 | [EMIM][TsO] | 1 | 1 | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 |
| 4 | [EMIM][MeSO$_3$] | 1 | 1 | 1 | 2 | 1 | 2 | 2 | 2 | 1 | 2 |
| 5 | [BMIM][BF$_4$] | 1 | 2[c] | 1 | 2[c] | 1[d] | 2 | 2 | 2 | 1 | 2 |
| 6 | [BMIM][Cl] | 1 | 1 | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 1 |

[a] Conditions: Table 1. [b] '1' and '2' as in Table 1. [c] Phase separation occurred, but only when the mixture contained less than 50 mol% ketone. [d] At reaction temperature the volume of the ionic liquid phase is increased by > 50% due to dissolution of the alcohol in the ionic liquid.

one phase with 2-octanol at reaction temperature, no phase separation with the 2-ketone occurred upon cooling to room temperature. Introduction of a nitrile function in the IL's cation led to the same effect as observed for the imidazolium based ILs: the IL is not able to dissolve the model substrate at reaction temperature anymore. Indeed, as reported in Table 1, neither 1-butylnitrile-1-methylpyrrolidinium bistriflimide ([CNBMPyr][Tf$_2$N]) nor 1-ethylnitrile-1-methylpyrrololidinium bistriflimide ([CNEMPyr][Tf$_2$N]) formed a homogeneous phase with 2-octanol (entries 24–25).

Next, other classes of ILs were evaluated, more specifically the betaine and choline based ILs (entries 26–29). The betaine based ILs are of interest because of their carboxylic acid group. In various Pd-catalyzed oxidation reactions, it has been found that a carboxylic acid function can facilitate the palladium reoxidation.[31] As evidenced in Table 1, the betaine and choline based ILs containing the hydrophobic [Tf$_2$N] anion proved miscible with 2-octanone (entries 26, 28). However, when choline is combined with a more polar anion, such as acetate or acesulfamate, phase separation with the ketone at

room temperature was observed (entries 28–29). In the case of choline acetate, a homogeneous phase with 2-octanol was formed. The acesulfamate anion decreased however the miscibility with both the alcohol and ketone making this IL less favourable. In general, it seems that irrespective of the cation, the ILs containing the [Tf$_2$N] anion did not exhibit the right phase behaviour.

For the aromatic alcohol substrates, with 1-phenylethanol as the model, the [Tf$_2$N] anion did not have the same negative effect on the phase behaviour of the IL. Both [BMIM][BF$_4$] and [BMIM][Tf$_2$N] were miscible with 1-phenylethanol at reaction temperature but did not mix with acetophenone at room temperature (Table 1, entries 14–15). When triflate as anion was assessed, the miscibility with the aromatic ketone increased dramatically (entry 16). A large number of ILs mixed perfectly not only with 1-phenylethanol at reaction temperature but also with acetophenone at room temperature, including the ammonium and imidazolium based ILs with long alkyl chains (entries 1-4), and most EMIM, BMMIM and BMPyr based ionic liquids (entries 8–13 and 18–22).

Summarizing, the IL screening revealed that seven ILs exhibit the ideal mixing behaviour with the model substrate 2-octanol and its 2-ketone oxidation product: [EMIM][CH$_3$CO$_2$], [EMIM][EtSO$_4$], [EMIM][TsO], [EMIM][MeSO$_3$], [BMIM][Cl], [BMIM][BF$_4$] and [Chol][CH$_3$CO$_2$]. In the case of aceto-phenone, only two ILs proved suitable: [BMIM][BF$_4$] and [BMIM][Tf$_2$N].

The 7 ILs suitable for 2-octanol oxidation were then subjected to a more in-depth miscibility test with a series of alcohols with varying chain length between C4 and C10. Mixing with the primary alcohol 1-octanol and the corresponding aldehyde was studied as well (Table 2). Due to the presence of an alcohol function, [Chol][CH$_3$CO$_2$] is probably not stable towards oxidation and hence this IL will not be addressed further. Table 2 reports that [EMIM][CH$_3$CO$_2$] exhibits the desired phase behaviour with the whole range of secondary aliphatic alcohols (entry 1). The other [EMIM] based ILs form 2 phases with the ketone upon cooling to room temperature in the series between 2-hexanol to 2-dodecanol (entries 2–4). However, they are not suitable for the catalytic oxidation of 2-butanol, due to the observed mixing of all ILs with butanone at room temperature. The same phase behaviour was observed for [BMIM][Cl] (entry 6). On the other hand, [BMIM][BF$_4$] demixes with all the investigated ketones at room temperature. Nevertheless, it did not form a homogeneous phase with 2-dodecanol at reaction temperature (entry 5). It should also be noted that in the case of 2-butanol and 2-hexanol, if the alcohol is converted for more than 50%, the ketone is not expelled spontaneously from the IL anymore, whereas at lower conversions phase separation occurred. For the primary 1-octanol, four ILs exhibited the desired phase behaviour with both alcohol and the corresponding ketone: [EMIM][EtSO$_4$], [EMIM][TsO], [EMIM][MeSO$_3$] and [BMIM][BF$_4$] (entries 2–5). [EMIM][CH$_3$CO$_2$] and [BMIM][Cl] formed one phase with octanal at room temperature (entries 1, 6).

The six ILs meeting the solubility criteria for 2-octanol were then evaluated for their chemical stability towards oxygen. A standard oxidation-stability test was designed for the ILs, by

exposing them to 30 bar O$_2$ for 24 h at 120 °C in the presence of palladium(II) acetate. Oxygen resistance was checked at the molecular level by $^1$H NMR as well as macroscopically by investigating colour and viscosity changes. For the six selected ILs no colour or viscosity changes could be observed. Furthermore, the $^1$H NMR spectra of the ILs before and after oxidation were identical, proving their oxidative stability (NMR spectra are provided in the ESI).†

### Catalytic oxidation of aliphatic alcohols in selected ionic liquid solvents

**Influence of the nature of the ionic liquid.** The alcohol oxidation was studied applying the IL media which displayed the appropriate mixing behaviour. Firstly, the influence of the type of IL on the catalytic oxidation of 2-octanol, as model aliphatic alcohol substrate, was explored using Pd(OAc)$_2$ as catalyst. Fig. 1 demonstrates that [BMIM][BF$_4$] and [EMIM][TsO] are the better reaction media, with 2-ketone yields of, respectively, 79 and 61%, compared to [EMIM][EtSO$_4$] and [EMIM][MeSO$_3$]. Using these ILs, phase separation was quick and spontaneous, allowing straightforward product analysis. Note that all oxidations performed in the various IL media were 100% selective towards the 2-ketone. No side-products such as ethers were observed. Remarkably, when the alcohol oxidation was performed in [BMIM][Cl] and [EMIM][CH$_3$CO$_2$], no phase separation occurred after cooling the reaction mixture to room temperature. Even upon extra ketone addition to the reaction mixture, the product was not expelled from the IL.

**Optimization of reaction conditions.** After identification of [BMIM][BF$_4$] as the optimal IL, the other reaction conditions were optimized for the 2-octanol oxidation. Fig. 2 shows that for a molar alcohol to catalyst ratio of 40 a reaction temperature of at least 120 °C is required to obtain acceptable 2-octanol conversion rates. Recall that octanol dissolution in [BMIM][BF$_4$] is not complete; rather the alcohol swells the IL phase. At 120 °C the alcohol was selectively converted for 79% towards 2-octanone. Presumably, the too low solubility of 2-octanol in the IL at temperatures below 120 °C, leading to slow kinetics, accounts for the low yields of 10 and 17%
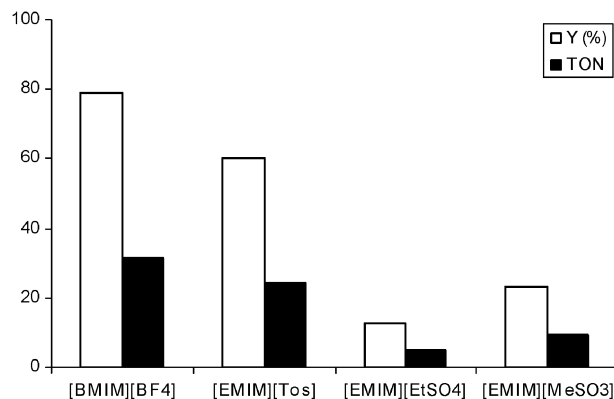


**Fig. 1** Influence of the nature of the ionic liquid on the alcohol oxidation: Y, ketone yield; TON = total turnover number (reaction conditions: 2-octanol (10 mmol), ionic liquid, mass ratio IL/alcohol = 1, Pd(OAc)$_2$ (molar ratio substrate/catalyst = 40, 120 °C, 10 bar O$_2$, 24 h).
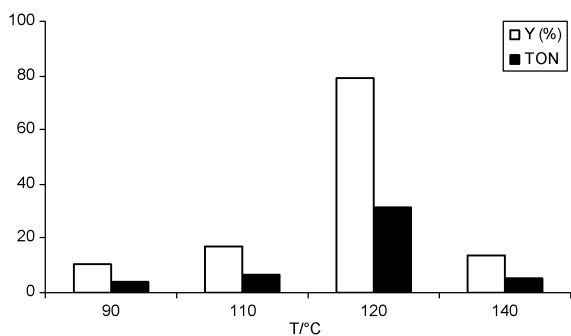
**Fig. 2** Influence of the reaction temperature on the Pd-catalyzed oxidation of 2-octanol (reaction conditions: 2-octanol (10 mmol), [BMIM][BF$_4$], mass ratio IL/alcohol = 1, Pd(OAc)$_2$ (molar ratio substrate/catalyst = 40), 10 bar O$_2$, 24 h; Y = yield; TON = turnover).

2-ketone at 90 and 110 °C, respectively. Similar observations were made for a substrate to catalyst ratio of 100. Interestingly, when further increasing the temperature from 120 °C to 140 °C, reaction rates decreased. This is probably due to the aggregation of the Pd clusters, which becomes more prominent at higher temperatures.

In Fig. 3 the evolution of the overall average turnover number (TON) with time is shown for a reaction at 120 °C. After high activity in the first few hours, the TON keeps steadily increasing, showing that stable activity can be maintained by the Pd catalyst dispersed in the IL phase, even at this high temperature.

As reported in Table 3, at 90 °C the 2-octanone yield increased from 4 to 22% and 36% when decreasing the molar IL to alcohol ratio (IL/A) from 1 to 0.5 and 0.1, respectively (entries 1–5). Apparently the poor substrate-catalyst contact at 90 °C due to too low substrate solubility in the IL was mitigated when lowering the IL/A ratio. This finding contrasts with the results obtained at 120 °C, at which temperature 2-octanol dissolves much more readily in [BMIM][BF$_4$]. In that case, an increase of the IL/A ratio had a positive influence on the conversion of the alcohol: employing an IL/A ratio of 0.25 gave a 2-octanone yield of 37%, where for a molar IL/A ratio of 1 the ketone product yield was 76% (entries 6–8). The opposite trend in function of the IL/A ratio observed at 120 °C could be explained by a better solubility of 2-octanol in
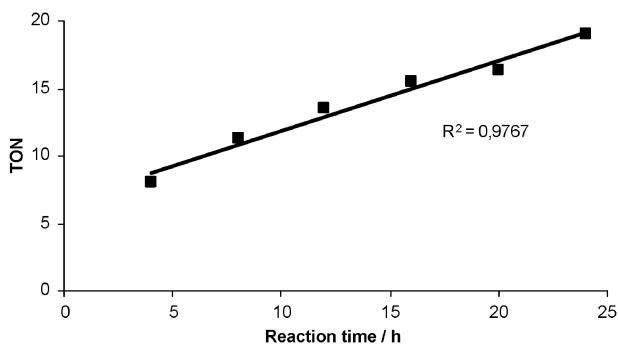


**Fig. 3** Evolution of the average turnover number in time (reaction conditions: 2-octanol (10 mmol), [BMIM][BF$_4$], mass ratio IL/alcohol = 1, Pd(OAc)$_2$ (molar ratio substrate/catalyst = 40), 120 °C, 30 bar O$_2$).

[BMIM][BF$_4$] at 120 °C compared to 90 °C, leading to a better substrate-catalyst contact. Indeed, whereas at 90 °C the ionic liquid phase is swollen but no complete mixing with the substrate takes place, nearly one homogeneous IL-substrate phase is formed at 120 °C. Thus with the substrate-catalyst contact at 120 °C not being dependent on the IL/A ratio, the positive effect of the ionic liquid on the reaction kinetics (e.g. catalyst stability) becomes more important as more ionic liquid is introduced into the reaction system. Interestingly, by increasing the amount of catalyst the effect of the IL/A ratio was reduced. Nevertheless the highest alcohol conversion was still observed for an IL/A ratio of 1, viz. 79% combined with a full 2-ketone product selectivity (entries 9–10). For 2-decanol oxidation in [BMIM][BF$_4$], the effect was not as straight-forward as for the 2-octanol, although the conversion of 2-decanol improved when the IL/A ratio was increased from 0.5 to 1 or 2 (entries 11–15). The optimal IL/A ratio identified was 0.82 in this case, yielding 87% of 2-decanone. By lowering the IL/A ratio to 0.25 the reaction mixture remained one homogeneous phase. It appears that the amount of IL is too small to spontaneously expel the ketone. Taking into account this result, the affinity of the IL for the ketone was checked, to investigate the leaching of IL into the product phase. The oxidation of 2-decanol (10 mmol) in [BMIM][BF$_4$] (IL/A = 1) at 120 °C was chosen as model reaction. The product phase, which was spontaneously expelled upon cooling of the reaction mixture to room temperature, was analyzed by NMR. Spiking tests indicated that the amount of IL leached in the product phase was less than 0.01%. Next, the effect of the catalyst loading was investigated. Table 3 (entries 3, 16–17) shows that at 90 °C and with an IL/A mass ratio of 0.5, a substrate to catalyst molar ratio (S C$^{-1}$) of 40 resulted in the highest 2-octanone yield (57%). A higher catalyst loading (S C$^{-1}$ = 20) probably provokes the aggregation of Pd particles, explaining the lower yield. As can be derived from Table 3 the oxygen pressure is also a significant reaction parameter (entries 18–28). For [BMIM][BF$_4$] at 120 °C, using a S C$^{-1}$ molar ratio of 100, the conversion of 2-octanol was close to zero when no external O$_2$ was introduced (entry 18). This could be expected because nearly no oxygen is available for the Pd re-oxidation. The yield of 2-octanone increases significantly when the O$_2$ pressure was increased: 2, 51 and 76% yield for 0, 5 and 10 bar of O$_2$, respectively (entries 8, 18–19). A further increase of the oxygen pressure to 20 bar and in particular 30 bar remarkably inhibited the reaction, with a ketone yield limited to 41% at 30 bar (entries 20–21). This is most likely due to palladium oxide formation, becoming more prominent at higher oxygen concentrations. The same observations were made when a S C$^{-1}$ molar ratio of 40 was applied (entries 10, 22–23). For reactions in [EMIM][EtSO$_4$], a similar oxygen pressure-catalytic activity relation was found (entries 24–28). However, in this IL the optimum oxygen pressure for 2-octanol oxidation was 30 bar. By further increasing the oxygen pressure, the ketone yield dropped to just 5%. In the case of [EMIM][MeSO$_3$], at 5 bar O$_2$ the ketone was obtained in only 9% yield, whereas at 10 bar, a ketone yield of 23% was obtained. Increasing the oxygen pressure to 20 and 30 bar did not further improve the yields (entries 29–32).

**Expanding the substrate scope.** After optimizing the reaction conditions for 2-octanol and 2-decanol, the oxidation of other alcohols was investigated. First, secondary aliphatic alcohols were used. At 120 °C, 10 bar of $O_2$ and after 24 h of reaction, the 2-ketone yields were determined for substrates with varying alkyl chain length. As reported in Table 4, 2-octanol and 2-decanol were the most reactive substrates, with ketone yields of 76 and 83%, respectively. Isolated yields of 2-butanol and 2-hexanol were substantially lower. One should however note that the difference in reactivity between the substrates may be overestimated because the oxidation experiments were performed under optimal conditions for 2-octanol and 2-decanol. In some reactions of 2-butanol and 2-hexanol, the overall conversion was higher than for the reactions shown in Table 4; but as no phase separation occurred (*cf*. Table 2), these results are not included. In the case of 2-dodecanol, the low yields can be explained in terms of low miscibility of 2-dodecanol with [BMIM][BF$_4$]. As shown in Table 2, even at 120 °C the 2-dodecanol and the IL form 2 phases without a significant swelling of the IL phase. With the catalyst in the IL phase, there is a pronounced substrate shortage in the catalyst phase.

Secondly, aromatic and primary aliphatic alcohol substrates were tested. The miscibility experiments indicated that two ILs, *viz*. [BMIM][BF$_4$] and [BMIM][Tf$_2$N] exhibited the right phase behaviour with 1-phenylethanol. Remarkably, when performing the 1-phenylethanol oxidation in the above mentioned ILs, no phase separation was observed upon cooling to room temperature or even to 0 °C. This can be ascribed to one of the following reasons: (1) the conversion may have been lower than 70%; note that 70% conversion corresponds with the standard mixture tested in the miscibility experiments; (2) side-products were formed which inhibit phase separation. Upon adding extra ketone to the mixture, no phase separation occurred, indicating that the too low conversion was not the cause for the monophasic nature of the reaction mixture containing the IL.

**Table 4** Influence of the alkyl chain length on the catalytic alcohol oxidation[a]

| Entry | Alcohol | $P(O_2)$/bar | Y(%)[b] | TON[c] |
|---|---|---|---|---|
| 1 | 2-Butanol | 10 | 11 | 11 |
| 2 | 2-Hexanol | 10 | 16 | 16 |
| 3 | 2-Octanol | 10 | 76 | 76 |
| 4 | 2-Decanol | 10 | 83 | 83 |
| 5 | 2-Dodecanol[d] | 10 | 21 | 21 |
| 6 | 2-Octanol | 30 | 66 | 66 |
| 7 | 2-Decanol | 30 | 64 | 64 |

[a] Reaction conditions: alcohol (10mmol), [BMIM][BF$_4$], mass ratio IL/alcohol = 1, Pd(OAc)$_2$ (molar ratio substrate/catalyst = 100), 120 °C, 24 h. [b] Yield of ketone. [c] Turnover number. [d] Reaction performed under constant pressure (in TOP multireactor).

**Table 3** Optimization of the reaction conditions for the catalytic oxidation of aliphatic alcohols[a]

| Entry | Ionic liquid | IL/A[b] | $P(O_2)$/bar | $T$/°C | $S/C^{-1}$[c] | Y(%)[d] | TON[e] |
|---|---|---|---|---|---|---|---|
| 1 | [BMIM][BF$_4$] | 0.1 | 10 | 90 | 100 | 36 | 36 |
| 2 | [BMIM][BF$_4$] | 0.2 | 10 | 90 | 100 | 23 | 23 |
| 3 | [BMIM][BF$_4$] | 0.5 | 10 | 90 | 100 | 22 | 22 |
| 4 | [BMIM][BF$_4$] | 0.75 | 10 | 90 | 100 | 19 | 19 |
| 5 | [BMIM][BF$_4$] | 1 | 10 | 90 | 100 | 4 | 4 |
| 6 | [BMIM][BF$_4$] | 0.25 | 10 | 120 | 100 | 37 | 37 |
| 7 | [BMIM][BF$_4$] | 0.5 | 10 | 120 | 100 | 47 | 47 |
| 8 | [BMIM][BF$_4$] | 1 | 10 | 120 | 100 | 76 | 76 |
| 9 | [BMIM][BF$_4$] | 0.5 | 10 | 120 | 40 | 72 | 29 |
| 10 | [BMIM][BF$_4$] | 1 | 10 | 120 | 40 | 79 | 32 |
| 11[f] | [BMIM][BF$_4$] | 0.25 | 30 | 120 | 40 | Np[g] | Np[g] |
| 12[f] | [BMIM][BF$_4$] | 0.5 | 30 | 120 | 40 | 55 | 22 |
| 13[f] | [BMIM][BF$_4$] | 0.82 | 30 | 120 | 40 | 87 | 35 |
| 14[f] | [BMIM][BF$_4$] | 1 | 30 | 120 | 40 | 64 | 26 |
| 15[f] | [BMIM][BF$_4$] | 2 | 30 | 120 | 40 | 78 | 31 |
| 16 | [BMIM][BF$_4$] | 0.5 | 10 | 90 | 40 | 57 | 23 |
| 17 | [BMIM][BF$_4$] | 0.5 | 10 | 90 | 20 | 21 | 4 |
| 18 | [BMIM][BF$_4$] | 1 | 0 | 120 | 100 | 2 | 2 |
| 19 | [BMIM][BF$_4$] | 1 | 5 | 120 | 100 | 51 | 51 |
| 20 | [BMIM][BF$_4$] | 1 | 20 | 120 | 100 | 71 | 71 |
| 21 | [BMIM][BF$_4$] | 1 | 30 | 120 | 100 | 41 | 41 |
| 22 | [BMIM][BF$_4$] | 1 | 20 | 120 | 40 | 71 | 71 |
| 23 | [BMIM][BF$_4$] | 1 | 30 | 120 | 40 | 66 | 26 |
| 24 | [EMIM][EtSO$_4$] | 1 | 5 | 120 | 40 | 11 | 4 |
| 25 | [EMIM][EtSO$_4$] | 1 | 10 | 120 | 40 | 13 | 5 |
| 26 | [EMIM][EtSO$_4$] | 1 | 20 | 120 | 40 | 12 | 5 |
| 27 | [EMIM][EtSO$_4$] | 1 | 30 | 120 | 40 | 21 | 9 |
| 28 | [EMIM][EtSO$_4$] | 1 | 40 | 120 | 40 | 5 | 2 |
| 29 | [EMIM][MeSO$_3$] | 1 | 5 | 120 | 40 | 9 | 4 |
| 30 | [EMIM][MeSO$_3$] | 1 | 10 | 120 | 40 | 23 | 9 |
| 31 | [EMIM][MeSO$_3$] | 1 | 20 | 120 | 40 | 25 | 10 |
| 32 | [EMIM][MeSO$_3$] | 1 | 30 | 120 | 40 | 23 | 9 |

[a] Reaction conditions: 2-octanol (10mmol), ionic liquid, Pd(OAc)$_2$, 24h. [b] Ionic liquid to alcohol mass ratio. [c] Substrate to catalyst molar ratio. [d] Yield of ketone. [e] Turnover number. [f] 2-decanol used as substrate. [g] No phase separation occurred upon cooling the reaction mixture to room temperature.

In the case of 1-octanol, a product phase was spontaneously expelled from [BMIM][BF$_4$] after cooling to room temperature (Table 5, entry 1). It should be noted that the oxidation did not stop at the aldehyde stage but further oxidation towards the carboxylic acid and ester (1-octyl octanoate) took place. The acid and ester were formed with a yield of 11 and 45%, respectively. This acid and ester formation from 1-octanol contrasts with results obtained for benzyl alcohol by Seddon *et al.*, who found that even in hydrophilic ionic liquid [BMIM][BF$_4$] no over-oxidation of benzyl alcohol due to the presence of water takes place, even upon extra introduction of water.[15] [EMIm][TsO] remained miscible with the product when the reactor was only loaded with 5 and 10 bar of oxygen; however further increasing the pressure to 20 and 30 bar caused phase separation, leading to acid and ester yields of 12 and 83% at 30 bar. Performing oxidation in [EMIM][MeSO$_3$] using 10 bar of oxygen, led to ester yields of 32%. Note that [EMIM][EtSO$_4$] did not phase separate from the products, irrespective of the oxygen pressure.

In Table 6, the results obtained under optimized reaction conditions are shown. In [BMIM][BF$_4$] at 120 °C, 10 bar of O$_2$ and a S C$^{-1}$ molar ratio of 40, 2-hexanol could be converted towards 2-hexanone with a yield of 48%. In the case of 2-octanol, 2-octanone was obtained in 79% yield in [BMIM][BF$_4$], compared to 63% in the absence of IL. Also for 2-decanol, the IL catalytic system was more active than for the neat alcohol solvent: at 120 °C and 30 bar of oxygen, 87% of ketone yield in [BMIM][BF$_4$] compared to only 39% in pure 2-decanol. These product yields are to the best of our knowledge the highest reported in literature for the oxidation of aliphatic alcohols in ILs. Our group previously published on the catalytic oxidation of alcohols in ILs, reporting a 2-octanol conversion of 43% in tetramethyl ammonium hydroxide and in the presence of RuCl$_3$.[19] As mentioned in the Introduction, most of the IL catalytic systems in the literature only dealt with the more reactive aromatic and allylic alcohols. Nevertheless two research groups investigated the activity towards non-activated secondary alcohols. Wang *et al.*, applying NaClO as the oxygen source, reported a conversion of 2-octanol of only 19%.[17] De Souza *et al.* converted 2-butanol with a yield of 61% in the presence of RuCl$_3$; however a reaction time of 70 h was required. In the case of 1-octanol, no conversion was observed at all.[16]

**Recycling and product separation.** In order to demonstrate the catalyst recycling, the catalyst immobilized in the ionic

**Table 5** Catalytic oxidation of the primary alcohol 1-octanol[a]

| Entry | Ionic liquid | P(O$_2$)/bar | Y(COOH) (%)[b] | Y(ester) (%)[c] |
|---|---|---|---|---|
| 1 | [BMIM][BF$_4$] | 10 | 11 | 45 |
| 2 | [EMIm][TsO] | 5 | Np[d] | Np[d] |
| 3 | [EMIm][TsO] | 10 | Np[d] | Np[d] |
| 4 | [EMIm][TsO] | 20 | 1 | 14 |
| 5 | [EMIm][TsO] | 30 | 12 | 83 |
| 6 | [EMIM][MeSO$_3$] | 10 | 0 | 32 |

[a] Reaction conditions: 1-octanol (10 mmol), ionic liquid, mass ratio IL/alcohol = 1, Pd(OAc)$_2$ (molar ratio substrate/catalyst = 40), 120 °C, 24 h. [b] Yield of carboxylic acid. [c] Yield of 1-octyl octanoate. [d] No phase separation occurred upon cooling the reaction mixture to room temperature.

**Table 6** Catalytic alcohol oxidation under optimized reaction conditions[a]

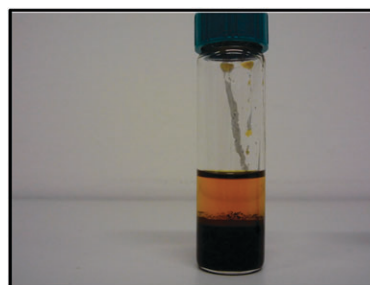| Entry | Alcohol | IL/A[b] | P(O$_2$)/bar | Y(%)[c] |
|---|---|---|---|---|
| 1 | 2-Hexanol[d] | 1 | 10 | 48 |
| 2 | 2-Octanol | 1 | 10 | 79 |
| 3 | 2-Octanol | 0[e] | 10 | 63 |
| 4 | 2-Decanol | 1 | 30 | 87 |
| 5 | 2-Decanol | 0[e] | 30 | 39 |

[a] Reaction conditions: alcohol (10 mmol), [BMIM][BF$_4$], Pd(OAc)$_2$ (molar ratio substrate/catalyst = 40), 120 °C, 10 bar O$_2$, 24 h. [b] Ionic liquid to alcohol mass ratio. [c] Yield of ketone. [d] 5 mmol 2-hexanol. [e] Reaction performed in absence of ionic liquid.

liquid phase was reused in the oxidation reaction. First, 2-octanol (10 mmol) was oxidized for 24 h at 120 °C in [BMIM][BF$_4$] under oxygen in the presence of Pd(OAc)$_2$. After allowing the reaction mixture to cool down to room temperature, phase separation occurred, and the product layer was isolated by decantation (see Fig. 4).

After removing the upper layer, the bottom IL layer was recycled. In the recycling experiment 2-decanol was oxidized. Different alcohols were used to exclude cross-contamination errors between the different recycles. As can be seen in Table 7, the selectivity remained 100% after recycling, while the conversion decreased from 79 to 70%. The decrease in conversion is not necessarily due to a decrease in catalytic activity since, unlike 2-octanol, 2-decanol is less reactive at 10 bar of oxygen compared to 30 bar O$_2$ (see Table 3). Additionally, the leaching problem in the recycled catalytic system was addressed by investigating the exact amount of palladium leaching by ICP (inductively coupled plasma) atomic emission analysis. After the recycling, leaching of palladium into the product phase amounted to less than 0.1% of the total amount of Pd supplied to the reaction.

## Conclusions

In conclusion, we developed a unique recyclable system for the oxidation of non-activated alcohols towards ketones. The choice of the ionic liquid was primarily governed by its ability to spontaneously expel the product, rather than by its effect on activity. From miscibility tests it emerged that only 6 out of 29 ionic liquids displayed the appropriate mixing behaviour for the oxidation reaction. Two ionic liquids resulted in high activity and selectivity values in the aliphatic alcohol oxidation in the presence of Pd(OAc)$_2$: 2-octanone yields of 79 and 61% in, respectively, [BMIM][BF$_4$] and [EMIM][TsO] are to our



**Fig. 4** Phase separation after catalytic oxidation of 2-octanol.

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**Table 7** Recycling of catalyst and ionic liquid in catalytic oxidation of alipathic alcohols[a]

| Run | Alcohol | C(%)[b] | S(%)[c] |
|-----|---------|---------|---------|
| 1 | 2-Octanol | 79 | 100 |
| 2 | 2-Decanol | 70 | 100 |

[a] Reaction conditions: alcohol (10 mmol), [BMIM][BF$_4$], mass ratio IL/alcohol = 1, Pd(OAc)$_2$ (molar ratio substrate/catalyst = 40), 120 °C, 120 °C, 10 bar O$_2$, 24 h. [b] Conversion of alcohol. [c] Selectivity to ketone.

knowledge the highest yields for aliphatic alcohols reported in ionic liquids. In the case of 2-decanol, even a yield of 86% could be achieved. The ionic liquids were miscible with the alcoholic substrates at reaction temperature, while a distinct phase separation of the corresponding ketone products was observed at room temperature. This mixing behaviour enabled the isolation of the reaction products by decantation without the need for an extracting solvent. Moreover, the ionic liquid mixture functioned as an immobilization medium for the catalyst which allowed efficient catalyst recycling.

## Acknowledgements

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