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# Surface-active ionic liquids in catalysis: Impact of structure and concentration on the aerobic oxidation of octanol in water

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## Abstract

We present design and synthesis of surface-active ionic liquids for the application in micellar catalysis. A series of 1-methyl-3-dodecylimidazolium based ionic liquids with variable core structures including dicationic and zwitterionic ones was synthesized and characterized. These surface-active ionic liquids were applied in the aerobic oxidation of aliphatic alcohols to carbonyl compounds. A strong dependence on the ionic liquid concentration and structure was identified, which is in accordance with the concepts of micellar catalysis. Optimum conditions for the oxidation of 1-octanol could be identified, and the use of surface-active ionic liquids strongly improved the reaction performance compared to pure water. Under optimized conditions, it was possible to isolate up to 75% of octanoic acid using only small amounts of surface-active ionic liquid in a 0.05 mM solution in water without further ligands.

*Keywords:* micellar catalysis, water, surfactants, ionic liquids, aerobic oxidation, Palladium

*2010 MSC:* 00-01, 99-00

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## Introduction

Solvent consumption accounts for a relevant part of the overall environmental impact of a chemical process. Replacing traditional volatile organic solvents with more benign ones such as water can be a key step towards the development of sustainable processes, although problems with substrate solubility may exist.[1] The addition of commercially available surfactants provides a powerful tool to overcome the solubility issue of many organic substrates in water, as the formation of aggregates in water enables the solubilization of reaction mixtures in water. Micelles or higher aggregates have the capability to drastically alter

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10 reaction rates, as the local concentration experienced by the reactants in the  
supramolecular assembly is higher than in a bulk solution.[2] Moreover, recent  
developments on the engineering of designer surfactants for a specific reaction  
showed a drastic impact on activity and selectivity through specific interactions  
between micelle, substrates and catalysts.[3]

15 For this purpose ionic liquids with a long alkyl chain have been recently  
intensely investigated. It has been demonstrated that ionic liquids with alkyl  
chains longer than 8 carbon atoms behave like amphiphiles and are able to form  
micelles in aqueous solution, which renders them ideal candidates as tailor-  
made surfactants for a number of applications.[4, 5] Micellar aggregates of  
20 surface-active ionic liquids can increase the solubility of organic compounds  
such as toluene in water[6], and are even suitable for the extraction of nat-  
ural compounds.[7] Moreover, the lipophilic core of ionic liquid aggregates in  
water can act as nanoreactor and exhibit strong kinetic effects on organic  
reactions.[8, 9, 10, 11] While research on the aggregation behaviour of ionic  
25 liquids in water focuses mainly on monocationic alkyl imidazolium based ionic  
liquids, studies on the adjustments of head group, side chain or counterion struc-  
ture have also been performed. This high tunability of ionic liquids provides a  
powerful tool for the design of the optimal environment for a specific reaction  
in water.[12].

30 Based on these considerations, we expanded our recent research on the design  
of surface-active ionic liquids for micellar catalysis towards the application in  
aerobic oxidations. In here, we report a study on the ligand free, unsupported,  
monometallic Pd catalysed oxidation of 1-octanol to octanoic acid in water with  
the aid of surface-active imidazolium-based ionic liquids and discuss impact of  
35 ionic liquid structure and concentration in water.

Oxidation reactions are among the most useful transformations and a key  
step for the synthesis of intermediates in organic chemistry. However, con-  
ventional methods relying on reagents such as Dess-Martin periodinane, Swern  
reagent, or the tetrapropylammonium perruthenate (TPAP)/N-methylmorpholine-  
40 N-oxide system exhibit low atom economy. These methods suffer from high  
waste production due to the by-products formed by the deactivation of the  
oxidizing agent after the reaction and are difficult to implement at industrial  
level.[13] As a result, research has focused on the development of more benign  
oxidations protocols, particularly on catalytic versions that operate under milder  
45 conditions and reduce waste.[14, 15] Among different proposed catalysts Palla-  
dium is a prime candidate, and homogenous catalysts based on Palladium with  
a number of ligands have been intensely investigated. Recently Muldoon et al.  
and Cámpora et al. reported a new series of N,O-ligated Pd(II) complexes based  
on pyridine-carboxylate and quinoline ligands which are competitive with the so  
50 far reported ones in term of turn-over frequency (TOF).[16, 17, 18] In general,  
dioxigen is considered as the most appealing oxidant used in combination with  
homogenous Palladium-catalysts as it is cheap, abundant and produces just wa-  
ter as by-product. However, due to safety issues, it should be used in diluted gas  
mixtures and/or in combination with non-flammable solvents such as water. As  
55 a consequence, Sheldon et al. reported highly efficient ligand systems based

on bathphenanthroline disulfonate, which allows to perform the Palladium-catalyzed oxidation of alcohols under aqueous conditions.[19, 20, 21] To obtain acceptable reaction rates for poor water soluble alcohols addition of co-solvents or additives were required. Recent research on Palladium-catalyzed aerobic  
60 oxidations of alcohols under aqueous conditions also suggest the use of water-soluble *N*-heterocyclic carbene ligands.[22] Han et al. reported the Palladium catalyzed aerobic oxidation of 1-heptanol in water using 1,3-dialkylimidazolium-based ligands with a quaternary ammonium moiety.[23] Alternatively, heterogeneous catalysts relying on Palladium-based nanomaterials have been reported  
65 for the oxidation of alcohols to carbonyl compounds.[24]

A number of aspects render surface-active ionic liquids in water an interesting alternative as reaction media in aerobic oxidations under aqueous conditions. Apart from the solubilization of the reaction mixture in water, surface-active ionic liquids, can, and have been, used to increase reaction rates, activity, and  
70 selectivity according to the concepts of micellar catalysis.[25, 26] Moreover, the impact of improved solubility is not limited to starting materials or catalyst species: Even though oxygen has generally low solubility in aqueous solutions, it has been reported that micelles can improve the oxygen concentration dissolved in the solution, therefore facilitating the oxidation of substrates solubilized in the  
75 aggregates.[27] Eventually, the role of the surface-active ionic liquid is not limited to the use as mere surfactant; moreover it can interact with the catalytically active species in oxidation reactions, either as *N*-heterocyclic carbene ligands or as stabilizer of in situ formed catalytically active Palladium nanoparticles.

## Materials and methods

### 80 *General*

Commercially available reagents and solvents were used as received from Sigma Aldrich unless otherwise specified. Doubly-distilled deionized water was obtained from a Millipore Milli-Q water purification system (Millipore, USA). All ionic liquids were dried for at least 48 h at room temperature and 0.01 mbar  
85 before use and were stored under an argon atmosphere.

For the characterization of the surface activity of the investigated ionic liquids the same procedure used in our previous work was followed.[9] Solutions at various concentration of the ionic liquids were prepared with doubly-distilled Millipore Milli-Q water and left under shaking at 360 min<sup>-1</sup> for 24 h at room  
90 temperature (RT) to equilibrate. For conductivity measurements, samples were previously equilibrated at (25 ± 0.1) °C in a HAAKE K15 thermostat. Conductivity measurement were performed on a Mettler Toledo Seven Excellence system, equipped with a InLAB 741-ISM electrode (cell constant  $\kappa = 0.105$ ). The conductimeter was calibrated with a standard KCl solution and two independent measurements were performed. The CMC was calculated as the  
95 intersection point of the two linear regimes in the conductivity/concentration graph. The degree of counter ion binding was calculated with the following equation  $\beta = 1 - \alpha$ , where  $\alpha$  is the degree of ionization and corresponds to the

ratio of the slopes between the two linear fragments of the conductivity curves.  
100 Surface tension was determined with the Du Noüy ring method on a Krüss manual tensiometer K6 at room temperature. Each measurement was repeated 5 times.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AC 200 or 400, using the solvent peak as reference. Infrared spectra were recorded on a Perkin-Elmer  
105 Spectrum 65 FT IR spectrometer equipped with a Specac MK II Golden Gate Single Reflection ATR unit. Gas chromatography analyses were carried out using a Thermo Scientific Focus gas chromatograph equipped with a BGB5 column BGB-5 (30 m x 0.25 mm i.d., 0.5 m film thickness) cross-bonded dimethyl polysiloxane capillary column and a FID detector. The following conditions were  
110 employed: Inlet temperature, 260 °C; split ratio 20; He carrier gas, 2 ml/min; detector temperature, 280 °C. The temperature program applied for the detection of octanal (*t<sub>r</sub>* = 5.2 min), 1-octanol (*t<sub>r</sub>* = 5.9 min), methyl benzoate (internal standard, *t<sub>r</sub>* = 6.2 min), octanoic acid (*t<sub>r</sub>* = 6.8 min) and octanoic acid octyl ester (*t<sub>r</sub>* = 9.9 min) was the following: Initial column temperature  
115 60 °C, heating to 170 °C at a rate of 15 °C/min, heating to 300 °C at a rate of 50 °C/min, final temperature held 5 minutes.

#### *Synthesis of ionic liquids*

Synthesis of [C<sub>12</sub>mim]X, with X = Cl<sup>-</sup> (**1**) and Br<sup>-</sup> (**3**): The halide-based imidazolium salts were synthesized following standard procedures, including the  
120 alkylation of *N*-methylimidazole or 1,2-dimethyl imidazole with the appropriate alkyl halide to yield the corresponding imidazolium halide that were repeatedly crystallized for purification. Details can be found in our previous work.[9]

*1-Dodecyl-2,3-dimethylimidazolium chloride (2)*. 1,2-Dimethylimidazole (7.99 g, 8.3 mmol) was placed in a three necks round bottom flask equipped with a  
125 condenser and an dropping funnel. 1-Chlorododecane (18.7 g, 9.1 mmol, 1.1 eq) were slowly added at room temperature. The reaction was left stirring at 100 °C for 4 days until NMR analysis showed complete conversion. Remaining volatiles were removed under reduced pressure, and the crude product was recrystallized from THF to obtain a colourless crystalline solid in 95% yield. <sup>1</sup>H-NMR (200  
130 MHz, CDCl<sub>3</sub>): δ(ppm) = 7.86 (1H, d, *J* = 1.90 Hz, NCH=CH), 7.49 (1H, d, *J* = 1.92 Hz, NCH=CH), 4.17 (2H, t, *J* = 7.41 Hz, CH<sub>2</sub>C<sub>11</sub>H<sub>23</sub>), 4.01 (3H, s, NCH<sub>3</sub>), 2.77 (3H, s, N=C-CH<sub>3</sub>), 1.75 (2H, t, *J* = 6.88 Hz, CH<sub>2</sub>CH<sub>2</sub>C<sub>10</sub>H<sub>21</sub>), 1.19 (18H, m, C<sub>2</sub>H<sub>4</sub>C<sub>9</sub>H<sub>18</sub>CH<sub>3</sub>), 0.81 (3H, t, *J* = 6.10 Hz, C<sub>11</sub>H<sub>22</sub>CH<sub>3</sub>). Analytical data was in accordance with literature.[28]

135 Synthesis of dicationic and zwitterionic surface-active ionic liquids: The remaining ionic liquids were synthesized through a two step procedure involving the alkylation of 1-dodecylimidazole, which was previously synthesized following a procedure reported in literature and distilled before use.[29]

*1,3-Bis(3-dodecanimidazolium-1-yl)methane dibromide (4)*. 1-Dodecylimidazole  
140 (4.32 g, 18.3 mmol, 2.1 eq) was dissolved in 15 ml of THF and 1.59 g of dibromomethane (9.1 mmol, 1 eq) were added at room temperature. The mixture

was heated to 65 °C for 5 days. After evaporation of the solvent, the product was dissolved in a small amount of CH<sub>2</sub>Cl<sub>2</sub> and precipitated by adding EtOAc. The product was obtained via filtration in 10% yield as a colourless solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 10.77 (s, 2H, -N-CH=N-), 8.95 (s, 2H, -N-CH<sub>2</sub>-N-), 7.53 (s, 2H, NCH=CH), 7.44 (s, 2H, NCH=CH), 4.22 (t, 4H, *J* = 7.64 Hz, CH<sub>2</sub>C<sub>11</sub>H<sub>23</sub>), 1.88 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>C<sub>10</sub>H<sub>21</sub>), 1.22-1.13 (m, 36H, C<sub>2</sub>H<sub>4</sub>C<sub>9</sub>H<sub>18</sub>CH<sub>3</sub>), 0.80 (t, 6H, *J* = 6.78 Hz, C<sub>11</sub>H<sub>22</sub>CH<sub>3</sub>). Analytical data was in accordance with literature.[30]

150 *1,3-Bis(3-dodecanimidazolium-1-yl)propane dibromide (5)*. 1-Dodecylimidazole (3.5 g, 14.8 mmol, 2.1 eq) were dissolved in 30 ml of THF and 1.49 g of 1,3-dibromopropane (7.4 mmol, 1 eq) were added at room temperature. The mixture was heated to 65 °C for 5 days. After evaporation of the solvent, the product was dissolved in a small amount of CH<sub>2</sub>Cl<sub>2</sub> and precipitated by adding  
155 EtOAc. The product was collected via filtration and obtained in 84% yield as a colourless solid. mp = 62.6 °C.  $\nu_{max}$ (cm<sup>-1</sup>) = 3132 (C-H Ar), 2919 (C-H), 2851 (C-H), 1571 (C=C), 1468 (C=C), 1161 (C-N). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 10.15 (s, N-CH=N-), 8.22 (s, 2H, -NCH=CH-), 7.30 (s, 2H, -NCH=CH-), 4.67 (t, 4H, *J* = 7.22 Hz, -N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N-), 4.20 (t, 4H, *J* = 7.48 Hz, CH<sub>2</sub>C<sub>11</sub>H<sub>23</sub>), 2.83 (quint, 2H, *J* = 7.25 Hz, -N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N-) 1.85 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>C<sub>10</sub>H<sub>21</sub>), 1.27-1.13 (m, 36H, C<sub>2</sub>H<sub>4</sub>C<sub>9</sub>H<sub>18</sub>CH<sub>3</sub>), 0.80 (t, 6H, *J* = 6.80 Hz, C<sub>11</sub>H<sub>22</sub>CH<sub>3</sub>). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ(ppm) = 136.46, 123.83, 121.60, 50.26, 46.71, 31.82, 30.88, 30.08, 29.52, 29.43, 29.32, 29.26, 28.92, 26.27, 22.60, 14.06.

165 *1,5-Bis(3-dodecanimidazolium-1-yl)pentane dibromide (6)*. 1-Dodecylimidazole (3.5 g, 14.27 mmol, 2.1 eq) was dissolved in 30 ml of THF and 1.64 g of 1,5-dibromopentane (7.13 mmol, 1 eq) were added at room temperature. The mixture was heated to 65 °C for 5 days. After evaporation of the solvent, the product was dissolved in a small amount of CH<sub>2</sub>Cl<sub>2</sub> and precipitated by adding  
170 EtOAc. The product was collected via filtration and obtained in 80% yield as a colourless solid. mp = 95.8 °C.  $\nu_{max}$ (cm<sup>-1</sup>): 3120 (C-H Ar), 2921 (C-H), 2852 (C-H), 1561 (C=C), 1459 (C=C), 1158 (C-N). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 10.31 (s, 2H, -N-CH=N-), 8.10 (s, 2H, NCH=CH-), 7.32 (s, 2H, -NCH=CH-), 4.44 (t, 4H, *J* = 7.06 Hz, -N-CH<sub>2</sub>-C<sub>3</sub>H<sub>6</sub>-CH<sub>2</sub>-N-), 4.23 (t, 4H, *J* = 7.46 Hz, CH<sub>2</sub>C<sub>11</sub>H<sub>23</sub>), 2.05 (m, 4H, -N-C<sub>2</sub>H<sub>4</sub>-CH<sub>2</sub>-C<sub>2</sub>H<sub>4</sub>-N-), 1.85 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>C<sub>10</sub>H<sub>21</sub>), 1.43 (m, 2H, -N-C<sub>2</sub>H<sub>4</sub>-CH<sub>2</sub>-C<sub>2</sub>H<sub>4</sub>-N-) 1.27-1.13 (m, 36H, C<sub>2</sub>H<sub>4</sub> C<sub>9</sub>H<sub>18</sub>CH<sub>3</sub>), 0.80 (t, 6H, *J* = 6.82 Hz, C<sub>11</sub>H<sub>22</sub>CH<sub>3</sub>). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ(ppm) = 136.61, 123.53, 121.54, 50.05, 49.01, 31.80, 30.23, 29.51, 29.42, 29.32, 29.24, 29.11, 28.92, 26.23, 22.59, 22.01, 14.05.

180 *4-(1-Dodecyl-3-imidazolium)butansulfonate (7)*. 1-Dodecylimidazole (3.17 g, 13.42 mmol, 1 eq) were dissolved in 5 ml of THF and a solution of 2.01 g 1,4-butansultone (14.76 mmol, 1.1 eq) in 5 ml of THF was added dropwise at 0 °C. The reaction mixture was warmed to room temperature and stirred for 6 days at 65 °C. The obtained precipitate was collected via filtration. The

185 crude product was washed with diethylether three times to obtain the product  
in 77% yield as a colourless solid. mp = 106.3 °C.  $\nu_{max}$ (cm<sup>-1</sup>): 3133 (C-H  
Ar), 2919 (C-H), 2848 (C-H), 1567 (C=C), 1469 (C=C), 1185 (C-N, S=O),  
1037 (S-O). <sup>1</sup>H-NMR (100 Hz, CDCl<sub>3</sub>):  $\delta$ (ppm) = 9.72 (s, 1H, -N-CH=N-),  
7.72 (s, 1H, -NCH=CH-), 7.23 (s, 1H, -NCH=CH-), 4.32 (t, 2H,  $J$  = 7.18 Hz,  
190 -N-CH<sub>2</sub>-C<sub>3</sub>H<sub>6</sub>-SO<sub>3</sub>), 4.15 (t, 2H,  $J$  = 7.38 Hz, CH<sub>2</sub>C<sub>11</sub>H<sub>23</sub>), 2.80 (t, 2H,  $J$  =  
7.46 Hz, -N-C<sub>3</sub>H<sub>6</sub>-CH<sub>2</sub>-SO<sub>3</sub>) 2.04 (q, 2H,  $J$  = 7.36 Hz, -N-CH<sub>2</sub>-CH<sub>2</sub>-C<sub>2</sub>H<sub>4</sub>-  
SO<sub>3</sub>) 1.80 (m, 4H, O<sub>3</sub>S-CH<sub>2</sub>-CH<sub>2</sub>-C<sub>2</sub>H<sub>4</sub>-N-CH-N-CH<sub>2</sub>CH<sub>2</sub>C<sub>10</sub>H<sub>21</sub>), 1.24-1.13  
(m, 18H, C<sub>2</sub>H<sub>2</sub>C<sub>9</sub>H<sub>18</sub>CH<sub>3</sub>), 0.80 (t, 3H,  $J$  = 6.82 Hz, C<sub>11</sub>H<sub>22</sub>CH<sub>3</sub>). <sup>13</sup>C-NMR  
(100 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) = 137.23, 123.08, 121.53, 50.86, 49.90, 49.38, 31.85,  
195 30.20, 29.56, 29.49, 29.37, 29.31, 29.29, 29.00, 26.28, 22.63, 22.16, 14.08.

*Poly(ethylene glycol) functionalized dicationic ionic liquid [C<sub>11</sub>im-PEG1000-  
C<sub>11</sub>im]Cl<sub>2</sub> 8*. The synthesis was performed adapting procedures already de-  
scribed in literature for the derivatization of PEG1000 to dichloro-PEG1000.[31,  
32] Subsequently 1.77 g of dichloro-PEG1000 (1.7 mmol, 1 eq) were mixed with  
200 0.93 g of 1-dodecylimidazole (3.9 mmol, 2.3 eq) and stirred for 4 days at 90 °C  
under argon. The product was washed several times with EtOAc and obtained  
as an orange viscose liquid in 89% yield. mp = 28.4 °C.  $\nu_{max}$ (cm<sup>-1</sup>): 2921  
(C-H), 2854 (C-H), 1563 (C=C), 1457 (C=C), 1103 (C-O-C). <sup>1</sup>H-NMR (400 Hz,  
CDCl<sub>3</sub>):  $\delta$ (ppm) = 10.54 (s, 2H, -N=CH-N-), 7.65 (s, 2H, -NCH=CH-), 7.21  
205 (s, 2H, -NCH=CH-), 4.60 (t, 4H,  $J$  = 4.42 Hz, -CH<sub>2</sub>-), 4.19 (t, 6H,  $J$  = 7.58  
Hz, -CH<sub>2</sub>-), 3.92 (t, 4H,  $J$  = 4.46 Hz, -CH<sub>2</sub>-), 3.60 3.53 (m, PEG), 1.83 (t, 4H,  
 $J$  = 6.36 Hz, CH<sub>2</sub>CH<sub>2</sub>C<sub>10</sub>H<sub>21</sub>), 1.18 (m, 41H, C<sub>2</sub>H<sub>4</sub>C<sub>9</sub>H<sub>18</sub>CH<sub>3</sub>), 0.88 (t, 6H,  $J$   
=6.84 Hz, C<sub>11</sub>H<sub>22</sub>CH<sub>3</sub>).

#### *Oxidation procedures*

210 *Representing procedure for the oxidation of 1-octanol at atmospheric pressure.*  
As general procedure to perform the oxidation of 1-octanol at 1 bar a stock so-  
lution of Pd(OAc)<sub>2</sub> (4.48 mg/ml) in EtOAc was prepared. This stock solution  
(1 ml) was placed in a 20 ml vial. The vial was placed under reduced pressure  
for 5 h to remove the solvent. Stock solutions of ionic liquids at different con-  
215 centrations were prepared in water that also contained the base K<sub>2</sub>CO<sub>3</sub> (13.8  
mg/ml). The stock solution of ionic liquid and base in water (2 ml) was added  
to a vial containing the catalyst, followed by 63.3  $\mu$ l of 1-octanol. A balloon  
filled with O<sub>2</sub> was placed on top of the vial with a syringe needle through a sep-  
tum. The vials were then placed in a pre-heated stirring block for the desired  
220 time and temperature. When the reaction was finished the vials were allowed  
to cool to room temperature before opening. An excess of 2 M HCl was added  
to neutralize the base and the product was extracted with 10 ml EtOAc. An  
aliquot of the organic layer was taken for GC analysis using methylbenzoate as  
internal standard.

225 *Representing procedure for the oxidation of 1-octanol under pressure.* A 40 ml  
autoclave was charged with catalyst 22.4 mg (0.1 mmol) and 138 mg (1 mmol)  
of K<sub>2</sub>CO<sub>3</sub>. The ionic liquid solution in water (10 ml) and 261 mg (2 mmol) of

1-octanol were added. The autoclave was loaded with air at the desired pressure and left stirring on a heating block for the desired time and temperature. The autoclave was cooled to room temperature prior to the release of the pressure. An excess of 2 M HCl was added to neutralize the base and the product was extracted with EtOAc. The organic fractions were collected together and diluted to 50 ml. An aliquote of this solution was taken for GC analysis using methylbenzoate as internal standard.

In order to isolate the product a different work-up procedure was followed: After pressure release an excess of base was added and remaining 1-octanol and by-products were extracted with EtOAc. Afterwards an excess of HCl was added and octanoic acid was successively extracted with EtOAc. The combined organic fractions were collected and diluted to 50 ml. An aliquot (0.4  $\mu$ l) of this solution was taken for GC analysis using methylbenzoate as internal standard. The remaining solution was dried over  $\text{Na}_2\text{SO}_4$ . Solvents were removed under reduced pressure to obtain octanoic acid in spectroscopically pure form.  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 11.32$  (s, 1H, COOH), 2.27 (t, 2H,  $J = 7.56$  MHz,  $-\text{CH}_2\text{-COOH}$ ), 1.56 (quin, 2H,  $J = 7.35$  MHz,  $-\text{CH}_2\text{-CH}_2\text{-COOH}$ ), 1.23 (m, 8H,  $\text{CH}_3\text{-C}_4\text{H}_8\text{-CH}_2\text{-}$ ), 0.80 (t, 3H,  $J = 6.88$  Hz,  $-\text{CH}_3$ ). Analytical data was in accordance with literature.[33]

## Results and Discussion

### *Design and synthesis of surface-active ionic liquids*

Based on our previous experience in cross-coupling chemistry and on recent literature data concerning Palladium-catalyzed oxidation, we focused on the use of imidazolium-based 1-alkylmethylimidazolium-based ionic liquids. These surface-active ionic liquids should not only act as amphiphiles to overcome solubility issues of the alcohol in water, but may directly act as ligands for Palladium. Consequently, a series of known and new surface-active ionic liquids based on the 1-dodecyl-3-methylimidazolium ( $[\text{C}_{12}\text{mim}]^+$ ) cation including dicationic and zwitterionic structures was synthesized adapting procedures already reported in literature.[34, 35, 29, 32] Different approaches were used and are depicted in Figure 1 .

In case of surface-active ionic liquids  $[\text{C}_{12}\text{mim}]\text{Cl}$  **1**,  $[\text{C}_{12}\text{mim}]\text{Br}$  **2** and  $[\text{C}_{12}\text{m}_2\text{im}]\text{Cl}$  **3** the direct alkylation of 1-methylimidazole or 1,2-dimethylimidazole with the desired dodecyl halides gave a straightforward access to the desired surface-active ionic liquids. The products could be obtained as colourless crystals in excellent yields after recrystallization from suitable solvents. The remaining surface-active ionic liquids were synthesized through a two step procedure relying on 1-dodecylimidazole as precursor: For the dicationic surface-active ionic liquids  $[\text{C}_{12}\text{im-C}_1\text{-C}_{12}\text{im}]\text{Br}_2$  **4**,  $[\text{C}_{12}\text{im-C}_3\text{-C}_{12}\text{im}]\text{Br}_2$  **5** and  $[\text{C}_{12}\text{im-C}_5\text{-C}_{12}\text{im}]\text{Br}_2$  **6** the corresponding dibromoalkane was used as alkylating agent with 2 equivalents of 1-dodecylimidazole. Precipitation in ethyl acetate afforded all products as colourless solids. Good yields were obtained for surface-active ionic liquids **5** and **6**, while in the case of **4** the high volatility of the starting material dibromomethane strongly limited the reaction results. The zwitterionic



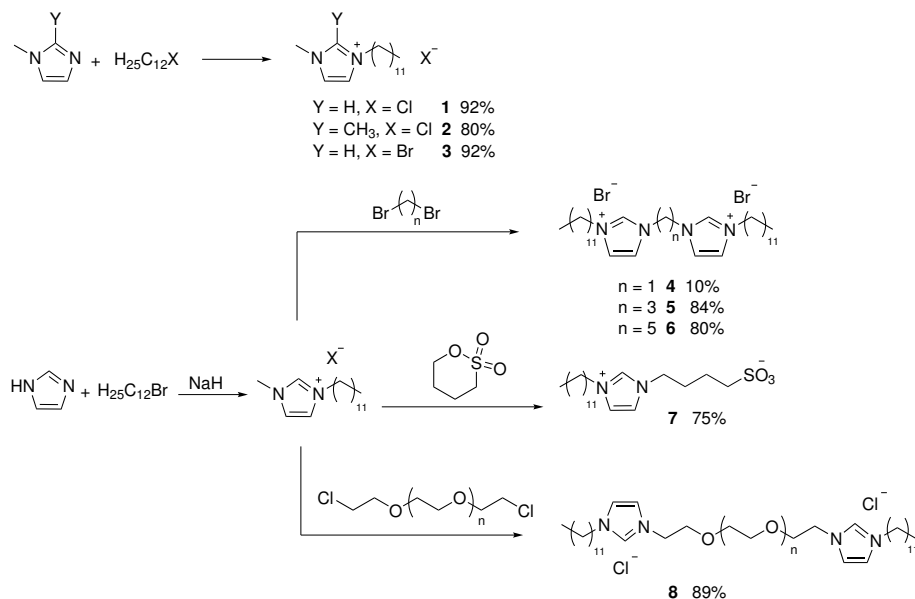


Figure 1: Synthesis of surface-active ionic liquids.

ionic liquid [C<sub>12</sub>im-C<sub>4</sub>-SO<sub>3</sub>] **7** was obtained through the ring opening reaction of 1,4-butane sultone with 1-dodecylimidazole to yield the product as a colourless solid in 77% yield. In order to synthesize [C<sub>12</sub>im-PEG1000-C<sub>12</sub>im]Cl<sub>2</sub> **8** an additional step for the derivatization of PEG1000 to the dichloro-PEG1000 prior to the alkylation with 1-dodecylimidazole was necessary. The product was obtained in the second step after washing with EtOAc as an orange wax in 89% yield.

#### Characterization of surface-active ionic liquids

The synthesized ionic liquids were characterized with regard to their surface activity. For this purpose critical micelle concentrations (CMC) were measured with two techniques, surface tension and conductivity, and results are depicted in Figure 2 and 3, and summarized in Table 1.

In general, imidazolium-based surfactants show a higher surface activity compared to the corresponding ammonium ones due to the delocalized charge on the imidazolium group.[36] The addition of a methyl group on the position 2 of the imidazolium ring slightly lowers the CMC. In addition, the anion plays a relevant role in the aggregation ability of surfactants, since it screens the electrostatic repulsion of the head groups in the micelles. Consequently, a less hydrated anion such as bromide favours micellization over chloride.[9]

Dicationic or gemini surfactants consist of two polar head groups with hydrophobic chains, covalently connected through a spacer.[35] In general, dicationic surfactants show a lower CMC than the monoatomic analogous and tend

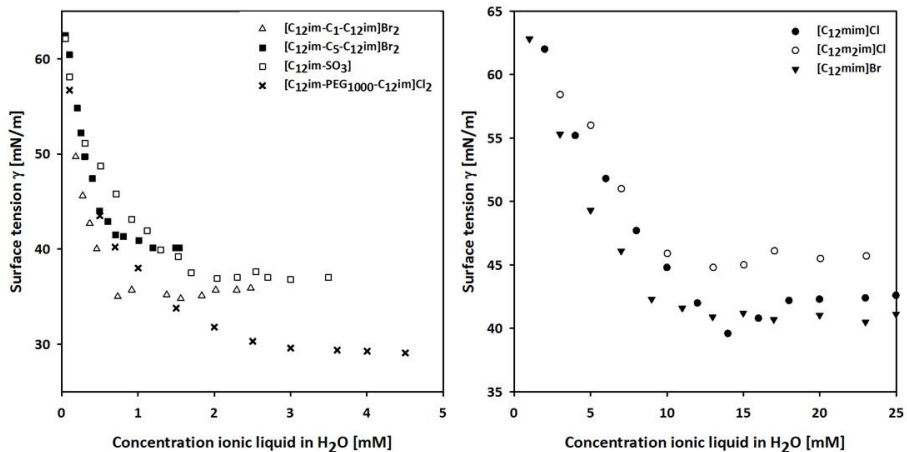


Figure 2: Surface tension of the investigated ionic liquids at 25 °C.

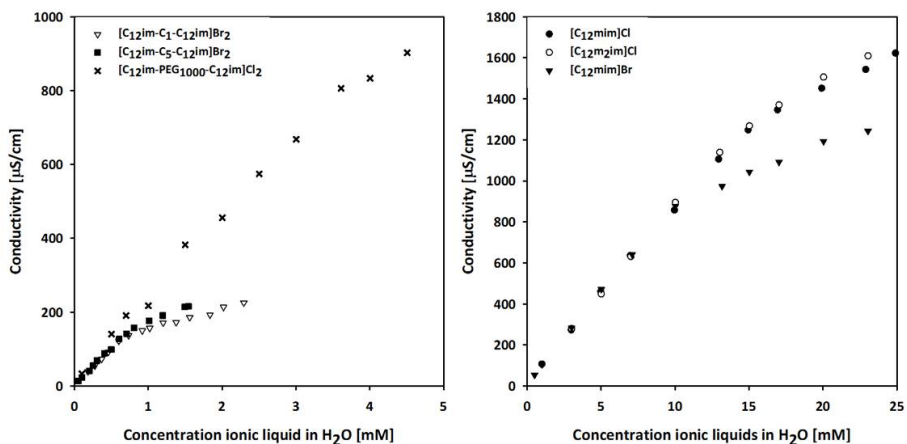


Figure 3: Conductivity of the investigated ionic liquids at 25 °C.

295 to aggregate forming vesicles like lipids.[30] The length of the spacer has a critical role in the determination of the flexibility of the molecule and hence on the formation of aggregates. As a consequence of these characteristic, a similar CMC was observed for the  $[C_{12}im-C_n-C_{12}im]Br_2$  series with  $n = 1$  and 5, while  $n = 3$  shows a minimum. A similar behaviour was already identified in a study on  $[C_{16}im-C_n-C_{16}im]Br_2$  dicationic surfactants with variable spacer length.[37]  
 300 Since zwitterionic surfactants are not suitable for conductivity measurement, the CMC of ionic liquid  $[C_{12}im-C_4-SO_3]$  **7** could only be determined by surface tension. Due to the overall neutral charge of the head group zwitterionic

305 surfactants have a higher surface activity compared to cationic surfactants, as can be seen in the comparison of surface-active ionic liquids [C<sub>12</sub>m<sub>2</sub>im]Cl and [C<sub>12</sub>im-C<sub>4</sub>-SO<sub>3</sub>]. Moreover, replacing the ammonium group of sulfobetaine with the imidazolium-based head group resulted in an decrease of the CMC, which is in accordance with literature data on cationic surfactants.[38]

Table 1: Critical micelle concentration (CMC) obtained by surface tension and conductivity for surface-active ionic liquids **1-8**.

Ionic Liquid	Surface tension [mM]	Conductivity [mM]
[C <sub>12</sub> mim]Cl <b>1</b>	13.25[9]	14.53[9]
[C <sub>12</sub> m <sub>2</sub> im]Cl <b>2</b>	10.33	13.75
[C <sub>12</sub> mim]Br <b>3</b>	9.29[9]	10.29[9]
[C <sub>12</sub> im-C <sub>1</sub> -C <sub>12</sub> im]Br <sub>2</sub> <b>4</b>	0.70	0.74
[C <sub>12</sub> im-C <sub>3</sub> -C <sub>12</sub> im]Br <sub>2</sub> <b>5</b>	0.53[39]	0.61[39]
[C <sub>12</sub> im-C <sub>5</sub> -C <sub>12</sub> im]Br <sub>2</sub> <b>6</b>	0.63	0.70
[C <sub>12</sub> im-C <sub>4</sub> -SO <sub>3</sub> ] <b>7</b>	1.67	-
[C <sub>12</sub> im-PEG1000-C <sub>12</sub> im]Cl <sub>2</sub> <b>8</b>	2.26	2.91

#### *Optimization of reaction parameters in the aerobic oxidation of 1-octanol*

310 With this set of surface-active ionic liquids with variable structure of the cationic head group in hand, we turned our attention towards the palladium-catalyzed aerobic oxidation of alcohols in water. We have chosen aliphatic inactivated alcohols, as these are less reactive in catalytic systems and notoriously difficult to oxidize. Our initial experiments focused on the optimization of reaction parameters for the oxidation of 1-octanol at atmospheric pressure. 315 Reactions were carried out using 2 ml of aqueous ionic liquid solution in magnetically stirred vials placed in a metal heating block. Oxygen was used as oxidizing agent and introduced in the system with a balloon through a septum. Results of the initial screening of reaction parameters are summarized in Table 3 .

320 After running the reaction for the indicated time, the crude reaction mixtures were analysed by GC. While traces of side products such as octanal and octyloctanoate ester below 5% were found, the oxidation proceeded smoothly towards octanoic acid as main product. As already suggested in literature, we found a strong influence of the base. Best results were obtained with potassium carbonate when used in a concentration range of 50-75 mol.% (Table 3, entry 2-3). 325 A higher or lower amount led to lower performance (Tab. 2 entry 1 and 4), while only traces of product were found when using NaOAc or the organic base DBU instead. The addition of acetic acid as sometimes suggested in literature did not benefit the reaction. When investigating the impact of catalyst loading, we found that at least 5 mol.% of Pd(OAc)<sub>2</sub> (Table 3, entry 2 and 330 7) were necessary in order to obtain satisfactory results. Surprisingly a higher amount did not further improve the yield of octanoic acid (Table 3, entry 8).

Table 2: Optimization of the reaction conditions for the oxidation of 1-octanol using 1 bar of O<sub>2</sub> as oxidizing agent.

Entry <sup>a</sup>	Temperature [°C]	Time [h]	Pd(OAc) <sub>2</sub> [mol.%]	K <sub>2</sub> CO <sub>3</sub> [mol.%]	Yield <sup>b</sup> [%]
1	100	18	5	20	10
2	100	18	5	50	64
3	100	18	5	75	65
4	100	18	5	100	48
5	100	18	5	50 <sup>c</sup>	< 5
6	100	18	5	50 <sup>d</sup>	< 5
7	100	18	2	50	< 5
8	100	18	10	50	56
9	100	18	2.5 <sup>e</sup>	50	58
10	25	18	5	50	< 5
11	50	18	5	50	< 5
12	80	18	5	50	42
13	100	6	5	50	< 5
14	100	12	5	50	48
15	100	24	5	50	71
16	100	48	5	50	64
17 <sup>f</sup>	100	18	5	50	5

<sup>a</sup> Reactions performed using 0.4 mmol of 1-octanol in 2 ml of a 5 mM [C<sub>12</sub>mim]Cl solution.

<sup>b</sup> Yield determined via GC analysis. Results are reported as average of two independent experiments.

<sup>c</sup> DBU used as base.

<sup>d</sup> NaOAc used as base.

<sup>e</sup> [Pd(allyl)Cl]<sub>2</sub> used as catalyst.

<sup>f</sup> Reactions performed with a 5 mM solution of CTAB instead of [C<sub>12</sub>mim]Cl solution.

Concerning the effect of temperature on the reaction, the reaction performed poorly at room temperature or 50 °C, while an increased temperature of at least 80 °C was required to improve the results (Table 3, entry 10-12). Eventually, the highest yield was obtained when running the oxidation at 100 °C for 24 hours using 5 mol.% Pd(OAc)<sub>2</sub> and 50 mol.% K<sub>2</sub>CO<sub>3</sub>, and up to 71% octanoic acid were formed (Table 3, entries 13-16). In order to compare surface-active ionic liquids with conventional surfactants, we also investigated the oxidation using 1-cetyltrimethylammonium bromide (CTAB) instead of [C<sub>12</sub>mim]Cl under the optimized conditions. It is important to highlight the superiority of surface active ionic liquids in micellar catalysis in comparison to conventional surfactants, in fact the use of CTAB afforded only 5% of the product (Table 3, entry 17). A similar effect has been observed by Cole-Hamilton et al. for

345 hydroformylation reactions, were imidazolium-based surfactants outperformed  
ammonium- or pyridinium-based structures.[40]

#### *Impact of ionic liquid concentration*

In order to gain a better understanding on the role of the ionic liquid in the  
system, different concentrations of ionic liquids [C<sub>12</sub>mim]Cl **1** were evaluated  
350 under the previously optimized conditions using 1 bar of O<sub>2</sub> as oxidizing agent.  
As can be seen in the results reported in Figure 4, a strong dependence of the  
yield of octanoic acid with regard to the surfactant concentration was found,  
which is in accordance with the concepts of micellar catalysis. Moreover, the  
presence of surface-active ionic liquids in the reaction mixture was essential, as  
355 only traces of the product could be identified in pure water as reaction media.  
As soon as the concentration of [C<sub>12</sub>mim]Cl **1** reached 1 mM the yield of oc-  
tanoic acid increased drastically to 50%. This suggests the formation of ionic  
liquid aggregates, although this concentration is below the CMC values for pure  
[C<sub>12</sub>mim]Cl **1** (Table 2). However, it can be assumed that the presence of cat-  
360 alyst and base renders the CMC to a lower value, which is in accordance with  
literature data studying salt effects on the aggregation of imidazolium-based  
ionic liquids.[41]

The best results were obtained with 5 mM [C<sub>12</sub>mim]Cl **1** which allowed to  
obtain 64% of octanoic acid yield. The concentration profile shows a maximum  
365 at 5 mM and, as it is usual for micellar catalysis, the performance decreases  
again above 15 mM. Interestingly a different profile was obtained in the case of  
[C<sub>12</sub>m<sub>2</sub>im]Cl **2** which allowed to obtain good yields even at high concentrations.  
The slightly decrease in octanoic acid yield at 10 and 15 mM for [C<sub>12</sub>m<sub>2</sub>im]Cl **2**  
can be balanced by the additional formation of the ester octyloctanoate, these  
370 were the only conditions at which 5-10% ester formation was identified.

Further studies showed that the catalyst Pd(OAc)<sub>2</sub> is actually decomposing  
during the reaction, as we observed the formation of heterogeneous Palladium  
aggregates forming during the oxidation (see ESI Figure S1). This suggest a  
different catalytically active species compared to Han et al., who reported that  
375 structurally related 1,3-dialkylimidazolium compounds containing a quaternary  
ammonium moiety act as NHC-ligand in this oxidation.

However, the formation of Palladium-based nanoparticles is not uncommon  
in this reaction. Pioneering work on Palladium nanoparticle mediated oxida-  
tions was conducted by Moiseev et al., who reported that a Pd giant cluster was  
380 able to catalyse the oxidation of lower alcohols to a series of different products  
including aldehydes, esters, anhydrides, carboxylic acids and acetals, while ben-  
zyl alcohols were oxidized to aldehydes. [42, 43] Different ligands have been used  
to stabilize Palladium nanoparticles. The previously mentioned neocuprine lig-  
and was also found to stabilize nanoparticles that were catalytically active in the  
385 oxidation of 2-hexanol, but also of some steroidal alcohols. [21, 24] Formation of  
Pd nanoparticles was mediated by the alcohol itself that acted as reducing agent  
in the presence of a co-solvent. Other stabilizing agents for Pd nanoparticles  
used in the oxidation of alcohols include polymers[44] such as polyethylenglycol

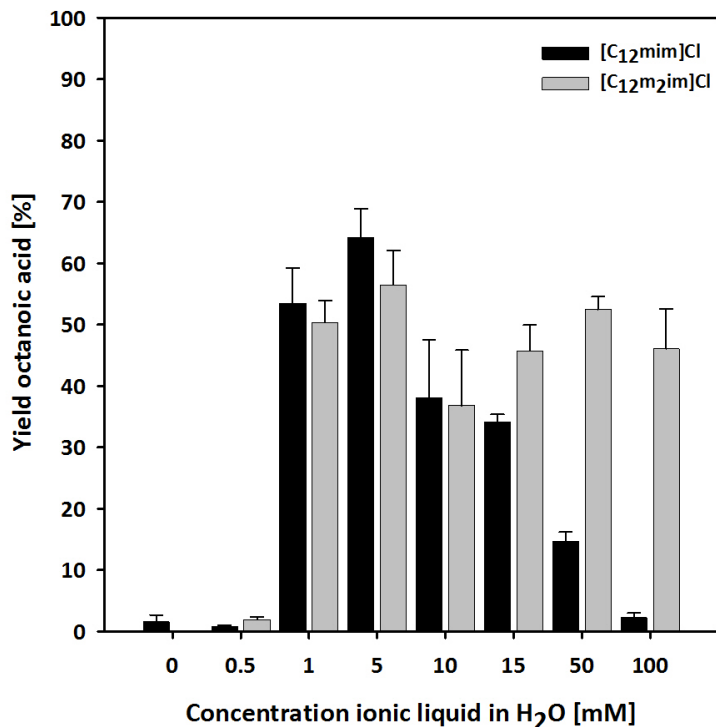


Figure 4: Results for the oxidation of 1-octanol performed with [C<sub>12</sub>mim]Cl (dark grey) and [C<sub>12</sub>m<sub>2</sub>im]Cl (light grey) at different concentrations. For reaction conditions see Tab.2.

[45, 46]. Due to the high tendency of Palladium nanoparticles to aggregate several reports on supported nanoparticles emerged lately. [47, 48] However their reactivity is mainly limited to allylic alcohols, while reports of their activity towards aliphatic alcohols is still scarce.[15] Different suggestions were made on the active species, as different species including Pd<sup>0</sup>, Pd<sup>+</sup> and Pd<sup>2+</sup> can be present on the surface of the nanoparticles at the same time, and the activity seems to be defined by the balance between PdO and metallic Pd.[49]

In case of surface-active ionic liquid [C<sub>12</sub>mim]Cl **1**, the catalytically active species seems to be dependent on the ionic liquid concentration. At high concentrations of [C<sub>12</sub>mim]Cl **1** no decomposition of the pre-catalyst was observed and poor yields were obtained, indicating that the pre-catalyst was stabilized by the ionic liquid. At lower concentrations, the pre-catalyst decomposes into catalytically active Pd aggregates. When using [C<sub>12</sub>m<sub>2</sub>im]Cl **2** the decomposition seems to be independent from concentration of ionic liquid, as constant yields were obtained over the entire concentration range investigated. The different performance of the two ionic liquids at high concentration indicates that the

405 co-existence of an homogenous and heterogeneous system, and it seems that the  
formation of a carbene on the imidazolium group plays a secondary role in the  
reaction mechanism. Moreover when the reaction mixture was warmed up in  
absence of the starting material 1-octanol no formation of Palladium aggregates  
but a light brown solution was obtained, suggesting that to initiate the catalytic  
410 cycle the alcohol is initially consumed to reduce Palladium.

#### *Impact of ionic liquid structure*

In order to improve the stabilization of the aggregates forming from the pre-  
catalyst decomposition, we expanded the range of surface-active ionic liquids to  
include dicationic and zwitterionic structures for the oxidation of 1-octanol to  
415 octanoic acid (Figure 5).

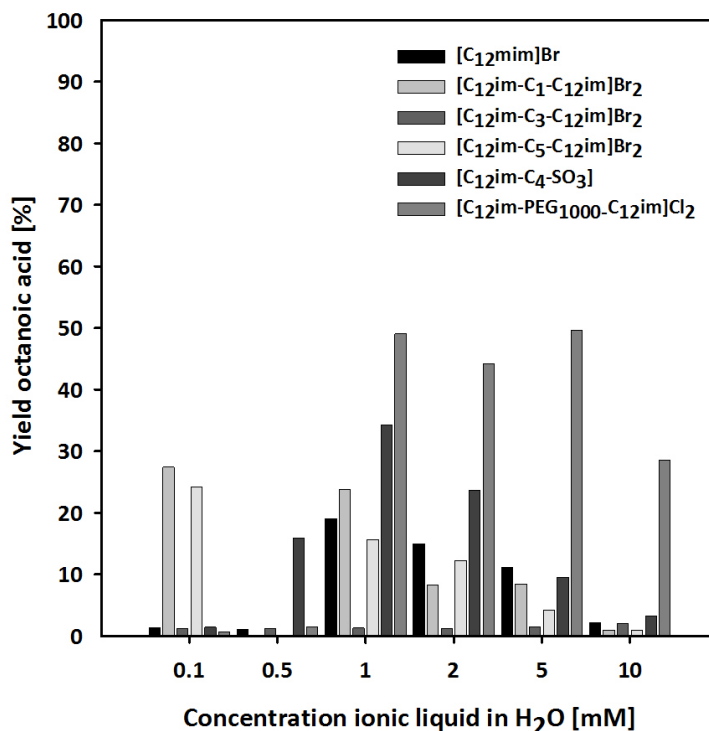


Figure 5: Octanoic acid yield for the oxidation of 1-octanol with the aid of different dicationic and zwitterionic ionic liquids. For reaction conditions see Tab 2.

In order to be able to compare the benefit of dicationic surface-active ionic liquids independently from the anion, [C<sub>12</sub>mim]Br **3** was tested initially. Only 19% of octanoic acid were formed at a concentration of 1 mM, suggesting that

[C<sub>12</sub>mim]Br is less efficient compared to [C<sub>12</sub>mim]Cl. Since dicationic surfactants usually present a lower CMC than the monocationic analogous[35], the dicationic structures [C<sub>12</sub>im-C<sub>1</sub>-C<sub>12</sub>im]Br<sub>2</sub> **4** and [C<sub>12</sub>im-C<sub>5</sub>-C<sub>12</sub>im]Br<sub>2</sub> **6** could improve the yield of octanoic acid to 27% and 24% respectively using a lower concentration of only 0.1 mM. The length of the spacer between the two imidazolium groups has however a strong influence: [C<sub>12</sub>im-C<sub>3</sub>-C<sub>12</sub>im]Br<sub>2</sub> **5** only afforded traces of the product. Dicationic imidazolium based surfactants have already been reported for the stabilization of silver nanoparticles in water, and the length of the spacer between the imidazolium head groups was found to influence the shape and the size of the formed nanoparticles. In particular very short bridges such as an ethylene bridge favoured the formation of elongated nanoparticles that could have a less advantageous active surface/volume ratio for catalytic applications.[37] Best results were obtained when testing the PEG-modified zwitterionic ionic liquid [C<sub>12</sub>im-PEG1000-C<sub>12</sub>im]Cl<sub>2</sub> **8** with 50% yield of octanoic acid in a concentration range between 2 and 5 mM. Reports of PEG containing surfactants have shown that they are efficient stabilizer for Pd nanoparticles in water. Examples on the application for hydrogenation and even for the aerobic oxidation of alcohols exist; however, their application towards the oxidation of aliphatic primary alcohols in water is still scarce.[50, 45, 32, 51, 52] Eventually, the zwitterionic surface-active ionic liquid [C<sub>12</sub>im-C<sub>4</sub>-SO<sub>3</sub>] **7** performed better than the dicationic ones reaching a maximum yield of 35%. Similar surface-active ionic liquids were found to stabilize Palladium nanoparticles in water via the formation of a double layer, and applications in hydrogenations were reported.[29] In any case, it is important to realize that the key to efficient catalysis lies in the appropriate stabilization. If stabilization of the catalytically active species is too high, this would inhibit the reaction, making it challenging to identify intermediate reaction conditions.

#### *From oxygen to air as oxidant*

While pure oxygen was used for the initial screening experiments, the use of air is clearly more attractive and adds considerably to the safety of the process. As can be seen in Figure 6 air could be used instead of oxygen, although a lower yield of 15% was obtained with 1 bar air. However, when increasing the pressure to 30 bar the yield could reach 40%. At this conditions the partial pressure of dioxygen is increased up to 6.2 bar. Further investigations on the optimization of the reaction conditions at higher pressure were made and confirmed conditions similar to those used at atmospheric pressure (see ESI Table S1). When comparing the influence of surface-active ionic liquid concentration with oxygen at atmospheric pressure and air at 30 bar it can be noticed that yields are shifted to lower concentration at high pressure compared to the ideal concentration range with oxygen at 1 bar (Figure 6). This is advantageous for the oxidation, as the required amount of the surface-active ionic liquid can be significantly reduced while maintaining the good performance

A similar behaviour was found for the best-performing surface-active ionic liquid [C<sub>12</sub>im-PEG1000-C<sub>12</sub>im]Cl<sub>2</sub> **8** (Table 4). While yields remained low with air under atmospheric pressure, a strong improvement was obtained using 30 bar



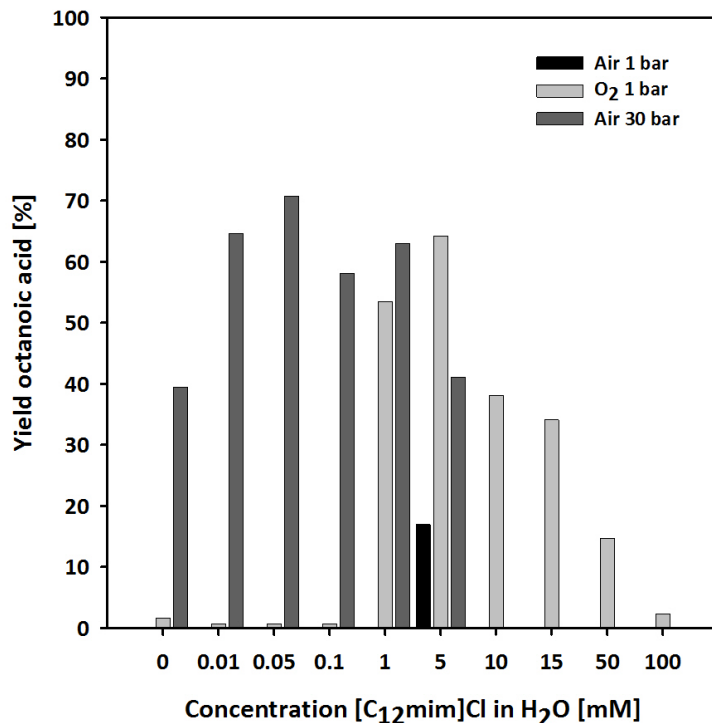


Figure 6: Comparison of the oxidation of 1-octanol to octanoic acid with [C<sub>12</sub>mim]Cl at different concentrations with oxygen and air.

of air with 0.05 mM as concentration. Eventually, it was possible to isolate up to 75% of the product octanoic acid using only small amounts of surface-active ionic liquid in a 0.05 mM solution without further ligands.

## Conclusion

Herein we presented the synthesis and characterization of a series of new and known surface-active 1-dodecyl-3-methylimidazolium-based ionic liquids including dicationic and zwitterionic structures and investigated their aggregation behaviour.[9, 36, 35, 37] These surface-active ionic liquids were applied as sole additive in the aerobic palladium-catalysed oxidation of 1-octanol to octanoic acid in water. Apart from pure oxygen, the system was also operating with air as a cheap, safe and benign oxidant which added considerable to the safety of the process. Among the tested surface-active ionic liquids the best results were obtained with the polyethylenglycol-based ionic liquid [C<sub>12</sub>im-PEG1000-C<sub>12</sub>im]Cl<sub>2</sub> in a 0.05 mM solution with a pressure of 30 bar air, and up to 75% yield of pure octanoic acid could be isolated. A strong influence on ionic liquid

Table 3: Comparison of the oxidation of 1-octanol to octanoic acid with oxygen and air.

Ionic liquid <sup>a</sup>	Concentration [mM]	Atmosphere	Pressure [bar]	Yield <sup>b</sup> [%]
[C <sub>12</sub> mim]Cl	5	oxygen	1	64
[C <sub>12</sub> mim]Cl	5	air	1	17
[C <sub>12</sub> mim]Cl	5	air	30	40
[C <sub>12</sub> mim]Cl	0.05	air	30	71 (63) <sup>c</sup>
[C <sub>12</sub> im-PEG1000-C <sub>12</sub> im]Cl <sub>2</sub>	5	oxygen	1	50
[C <sub>12</sub> im-PEG1000-C <sub>12</sub> im]Cl <sub>2</sub>	5	air	1	14
[C <sub>12</sub> im-PEG1000-C <sub>12</sub> im]Cl <sub>2</sub>	0.05	air	30	75 (75) <sup>c</sup>

<sup>a</sup> Reactions performed using 2 mmol of 1-octanol in 10 ml of ionic liquid solution.

<sup>b</sup> Yield determined via GC analysis.

<sup>c</sup> Isolated yield reported in brackets.

structure and concentration was found, suggesting that the surface-active ionic liquids play a dual role as surfactant and stabilizer for the catalytically active species as it has been also observed for Palladium-catalysed cross-coupling in water.[29] Optimization of reaction parameters allowed to obtain octanoic acid in good yields, and a number of critical aspects offer advantages to currently available processes for the oxidation of non-activated alcohols in micellar media.

According to previously reported protocols and methods, the oxidation of alcohols in micellar catalysis still relies on the use of stoichiometric organic oxidants [46, 53] or metal oxides as oxidant [54, 55, 56]. Moreover literature deals mainly with activated or short alkyl chain alcohols, which have a considerably higher solubility in water [1, 57, 58]. In our system even a small amount of imidazolium based surface-active ionic liquids was very effective in comparison to an ammonium-based surfactant, both in terms of surface activity and for the application in the oxidation of the scarcely reactive primary aliphatic alcohol 1-octanol to octanoic acid. Surface-active ionic liquids significantly improved the yield obtained with pure water, as they could not only overcome the limited solubility of octanol in water but were also able to stabilize the Pd-catalyst in such an extent that no additional ligands or support were required.[48, 24].

Our current research aims to elucidate the interplay between imidazolium-based surface-active ionic liquid and catalytically active species in this reaction. More studies concerning the concentration-dependent formation and stabilization of nanoparticles in surface-active ionic liquids for aqueous oxidations and cross coupling reaction are currently under way.

## Acknowledgement

Financial support by the Austrian Science Fund (FWF project P25504-N28) is gratefully acknowledged.

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## Figure Captions

Figure 1 : Synthesis of surface-active ionic liquids.

Figure 2 : Surface tension of the investigated ionic liquids at 25 °C.

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Figure 3 : Conductivity of the investigated ionic liquids at 25 °C.

Figure 4 : Results for the oxidation of 1-octanol performed with [C<sub>12</sub>mim]Cl (dark grey) and [C<sub>12</sub>m<sub>2</sub>im]Cl (light gray) at different concentrations. For reaction conditions see Tab.2.

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Figure 5 : Octanoic acid yield for the oxidation of 1-octanol with the aid of different dicationic and zwitterionic ionic liquids. For reaction conditions see Tab 2.

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Figure 6 : Comparison of the oxidation of 1-octanol to octanoic acid with [C<sub>12</sub>mim]Cl at different concentrations with oxygen and air.

## Tables

Table 1: Critical micelle concentration (CMC) obtained by surface tension and conductivity for surface-active ionic liquids **1-8**.

Ionic Liquid	Surface tension [mM]	Conductivity [mM]
[C <sub>12</sub> mim]Cl <b>1</b>	13.25[9]	14.53[9]
[C <sub>12</sub> m <sub>2</sub> im]Cl <b>2</b>	10.33	13.75
[C <sub>12</sub> mim]Br <b>3</b>	9.29[9]	10.29[9]
[C <sub>12</sub> im-C <sub>1</sub> -C <sub>12</sub> im]Br <sub>2</sub> <b>4</b>	0.70	0.74
[C <sub>12</sub> im-C <sub>3</sub> -C <sub>12</sub> im]Br <sub>2</sub> <b>5</b>	0.53[39]	0.61[39]
[C <sub>12</sub> im-C <sub>5</sub> -C <sub>12</sub> im]Br <sub>2</sub> <b>6</b>	0.63	0.70
[C <sub>12</sub> im-C <sub>4</sub> -SO <sub>3</sub> ] <b>7</b>	1.67	-
[C <sub>12</sub> im-PEG1000-C <sub>12</sub> im]Cl <sub>2</sub> <b>8</b>	2.26	2.91

Table 2: Optimization of the reaction conditions for the oxidation of 1-octanol using 1 bar of O<sub>2</sub> as oxidizing agent.

Entry <sup>a</sup>	Temperature [°C]	Time [h]	Pd(OAc) <sub>2</sub> [mol.%]	K <sub>2</sub> CO <sub>3</sub> [mol.%]	Yield <sup>b</sup> [%]
1	100	18	5	20	10
2	100	18	5	50	64
3	100	18	5	75	65
4	100	18	5	100	48
5	100	18	5	50 <sup>c</sup>	< 5
6	100	18	5	50 <sup>d</sup>	< 5
7	100	18	2	50	< 5
8	100	18	10	50	56
9	100	18	2.5 <sup>e</sup>	50	58
10	25	18	5	50	< 5
11	50	18	5	50	< 5
12	80	18	5	50	42
13	100	6	5	50	< 5
14	100	12	5	50	48
15	100	24	5	50	71
16	100	48	5	50	64
17 <sup>f</sup>	100	18	5	50	5

<sup>a</sup> Reactions performed using 0.4 mmol of 1-octanol in 2 ml of a 5 mM [C<sub>12</sub>mim]Cl solution.

<sup>b</sup> Yield determined via GC analysis. Results are reported as average of two independent experiments.

<sup>c</sup> DBU used as base.

<sup>d</sup> NaOAc used as base.

<sup>e</sup> [Pd(allyl)Cl]<sub>2</sub> used as catalyst.

<sup>f</sup> Reactions performed with a 5 mM solution of CTAB instead of [C<sub>12</sub>mim]Cl solution.

Table 3: Comparison of the oxidation of 1-octanol to octanoic acid with oxygen and air.

Ionic liquid <sup>a</sup>	Concentration [mM]	Atmosphere	Pressure [bar]	Yield <sup>b</sup> [%]
[C <sub>12</sub> mim]Cl	5	oxygen	1	64
[C <sub>12</sub> mim]Cl	5	air	1	17
[C <sub>12</sub> mim]Cl	5	air	30	40
[C <sub>12</sub> mim]Cl	0.05	air	30	71 (63) <sup>c</sup>
[C <sub>12</sub> im-PEG1000-C <sub>12</sub> im]Cl <sub>2</sub>	5	oxygen	1	50
[C <sub>12</sub> im-PEG1000-C <sub>12</sub> im]Cl <sub>2</sub>	5	air	1	14
[C <sub>12</sub> im-PEG1000-C <sub>12</sub> im]Cl <sub>2</sub>	0.05	air	30	75 (75) <sup>c</sup>

<sup>a</sup> Reactions performed using 2 mmol of 1-octanol in 10 ml of ionic liquid solution.

<sup>b</sup> Yield determined via GC analysis.

<sup>c</sup> Isolated yield reported in brackets.