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Further investigation of the biodegradability of imidazolium ionic liquids

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In continuation of our earlier investigations, this report presents a rationale behind the design of a series of imidazolium based ionic liquids and their biodegradation using the CO_2 headspace test (ISO 14593 method, OECD 310). The effect on biodegradability of these salts through variation of the *N*-substituted side chains of imidazolium ions was examined further through incorporation of various functional groups and increased alkyl chain lengths. A series of anions containing moieties known to be biodegradable were also incorporated into a number of imidazolium based salts and examined in a similar fashion.

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Introduction

Ionic liquids (ILs) initially attracted the attention of chemists because of the advantages they offer in electrochemistry, separation processes and heterogeneous catalysis.[1] The properties of ILs, such as good chemical and thermal stability, lack of vapor pressure and good solubility for a range of organic, inorganic, organometallic compounds and even gases, have presented several avenues of interest for chemists to explore.[2] Their architectural flexibility has broadened the scope of their applications to include their use in materials design,[3] immobilized phases,[4] catalyst anchoring,[5] functionalized phases,[6] supported synthesis,[7] to name only a few. ILs are now among chemists' first picks as unconventional reaction media, not only because of their blend of unique, tunable properties, but also because of their commercial availability and ease of synthesis and handling. Although the aforementioned solvent attributes have helped chemists to develop many green, operationally safer processes, their impact on the environment has been a topic of discussion.[8] In spite of the recent debates on their volatility,[9] it is thought that ILs would not pose any threat to air quality under operational conditions of typical chemical processes. Their impact on water and soil quality is certainly a concern to environmental chemists, mainly because these effects have not been evaluated to any great extent and nor are they predictable.[10] Several reviews and reports expressing the importance of conscientious design of chemicals have appeared over the last few years.[11] For new chemicals, such as ILs, it is important to evaluate their ecological impact while assessing them for other properties applicable for their end use.[12]

Many research groups, including ours, have considered the environmental effects of ILs by measuring their toxicity.[13] However, it is important to note that toxicity and biodegradability need not always be mutually exclusive.[11b] A toxic substance with good biodegradability is not necessarily as much of a concern as a non-toxic, recalcitrant substance. This is because the latter may persist and bio-accumulate exerting long term chronic effects. Biodegradation is a natural process involving a collective effort of different microorganisms breaking down the complex organic molecules into biomass and/or inorganic compounds, such as carbon dioxide and water. Hence, a biodegradable, but toxic, substance may exert an acute effect upon exposure to it but will be rendered non-toxic upon its biodegradation into biomass and/or inorganic compounds as mentioned above. Once released in water or soil, both the environmental and structural factors influence the mineralization of a substance. The biodegradation data obtained for any compound greatly depends on both the physiological and catabolic nature of the microbial population present in the medium.

The CO_2 headspace test (ISO 14593, OECD 310) was used to assess the biodegradability of ILs prepared in this investigation. The methods used for evaluating ready biodegradability are based on measuring non-specific parameters like dissolved organic carbon, biochemical oxygen demand and CO_2 production. The ready biodegradability tests are performed under stringent conditions of low microbial density and high concentrations of the test substance (as the only source of carbon for the microorganisms). A substance attaining the pass level in these tests at a certain rate after termination of the lag phase may be classified as "readily biodegradable". The pass level depends on the analytical parameter measured. A substance passes the CO_2 headspace test (OECD 310) when at least 60% of the theoretical carbon dioxide is liberated within the first 28 days. A positive result in a test for ready biodegradability can be considered as indicative of rapid and ultimate degradation in most environments including waste water treatment plants.

Our earlier work on biodegradable ILs was focused on investigating the environmental impact of imidazolium based ILs.[14] Although the conventional and most commonly used imidazolium based ILs are recalcitrant, higher biodegradability can be attained by suitably modifying the structure of the cation and anion. Integrating the ester side chain derived from C_5 alcohol and C_2 acid on the imidazolium cation helped to

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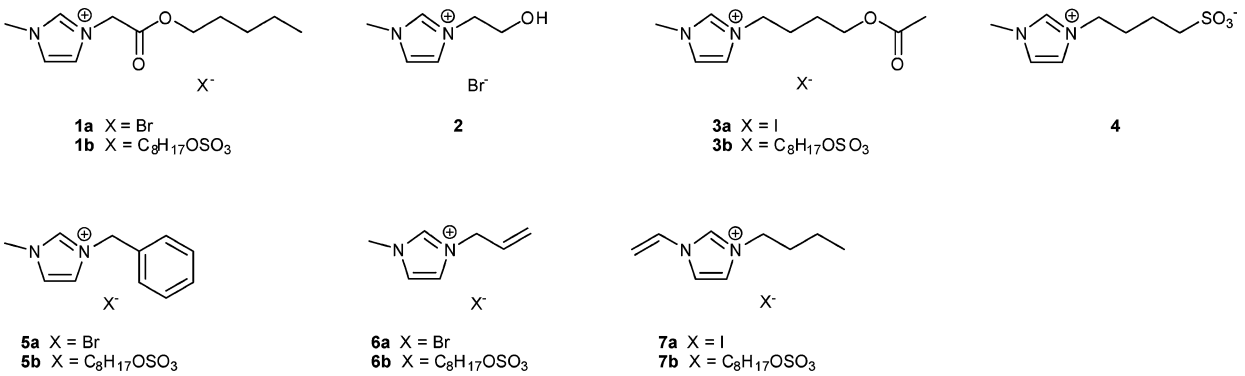

1a X = Br
1b X = $C_8H_{17}OSO_3$

2

3a X = I
3b X = $C_8H_{17}OSO_3$

4

5a X = Br
5b X = $C_8H_{17}OSO_3$

6a X = Br
6b X = $C_8H_{17}OSO_3$

7a X = I
7b X = $C_8H_{17}OSO_3$

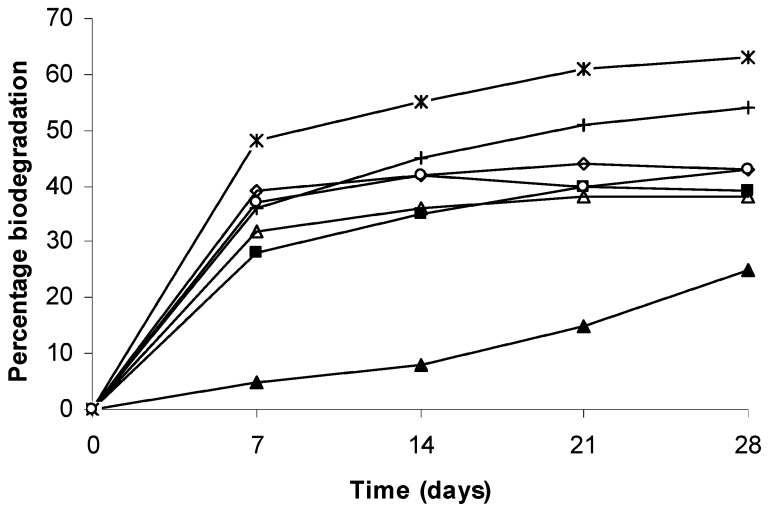

Fig. 1 Effect of cation modifications on percentage biodegradation, **1a** (■), **1b** (✳), **3a** (▲), **3b** (+), **5b** (△), **6b** (◇),**7b** (○). Compounds **2**, **4**, **5a**, **6a** and **7a** underwent <5% biodegradation (data not plotted).

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achieve higher biodegradation values.[14a,c] The ester group was chosen because esterases are not only the most common enzymes but are also known to offer broad substrate specificity. The studies carried out on the pyridinium based ILs have indicated that perhaps the presence of an ester group is necessary to obtain acceptable levels of biodegradability; however, unlike the imidazolium ring,[15] the pyridinium core is not refractory.[15,16] In the case of the imidazolium based salts/ILs, the C_8 based alkyl sulfate anion has been a preferred choice, since it has the optimal alkyl chain length to achieve high biodegradability while retaining good solvent properties.[14a,c]

Results and discussion

We noted that although imidazolium based ILs have been modified in various ways to enhance their biodegradability, many structural features that could potentially enhance the biodegradability of this class of ILs have yet to be explored, particularly with regards to modification of the anion. Hence, we aimed to synthesize and test a heretofore uninvestigated series of the imidazolium based ILs/salts for biodegradability. Some simple targets that are already known in the literature, or those that can be easily synthesized starting with commercially known starting materials, were of particular interest. In selecting the targets, we abided by the "rules of thumb" for biodegradability as described in a review article by Boethling *et al.*[11b] Some materials and anions derived from compounds with known toxicological profiles were also subjected to the biodegradation test. 3-Methyl-1-(pentoxycarbonylmethyl)imidazolium octylsulfate (**1b**), which was previously shown to meet the requirement for classification as 'readily biodegradable' as determined by the CO_2 headspace test,[14c] was included for comparative purposes in this study.

Although the biodegradability of the dialkylimidazolium ILs with ester containing side chains have been investigated, in all cases this side chain was derived from an α-halo ester which afforded the corresponding alkyloxycarbonylmethyl imidazolium salt.[14] The biodegradability of imidazolium ILs that bear either an alcohol functionality on the alkyl side chain or on the esters derived from them (*i.e.* with the ester functionality reversed) has yet to be examined. The presence of oxygen in the structure increases the tendency of a substance to metabolize. The quaternary salt **2** contains a primary alcohol group on the alkyl side chain. Both the quaternary iodide **3a** and the quaternary bromide **2** were conveniently derived from commercially available starting materials. Whereas **2** did not show significant biodegradation, **3a** showed reasonably good

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tendencies to biodegrade under the test conditions. Compound **3a** showed biodegradation at 25% after the standard 28 day incubation period (Fig. 1). Notably, the cation in both **3a** and **3b** can be regarded as a derivative of C_4 alcohol with a C_2 acid, and hence, possesses skeletal similarity to the cation of imidazolium based biodegradable ILs investigated earlier by our group.[14a] The replacement of the iodide in **3a** with the octyl sulfate anion, as in **3b**, increased the biodegradation to 54%. This is relatively close to the acceptable 60% level for a substance to be classified as readily biodegradable by this test.

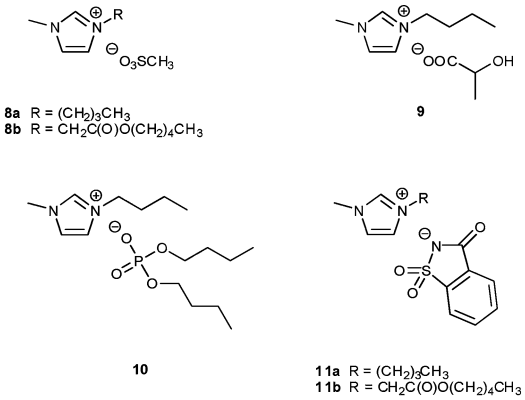
The zwitterionic imidazolium compound **4**, which was readily obtained by the *N*-alkylation of 1-methylimidazole with 1,4-butane sultone, did not show appreciable biodegradation. Compound **4** is a precursor for the synthesis of sulfonic acid containing imidazolium based task specific ILs. Whereas we have previously shown that the presence of alkyl sulfate anions paired with *N*,*N*-disubstituted imidazolium ions enhanced biodegradability,[14] it is evident that incorporation of the anionic sulfonate group on the alkyl side chain of the imidazolium cation does not help improve the biodegradation.

It is known that the incorporation of the phenyl ring in some molecules helps to improve their biodegradability,[11b] mainly because the phenyl ring is prone to attack by the oxygenases that oxidize the ring facilitating other metabolic processes that lead to mineralization. However, the quaternization of 1-methylimidazole with benzyl bromide yielded the quaternary bromide **5a** which showed <5% biodegradability after 28 days. The corresponding octyl sulfate salt **5b** showed biodegradation at 38%, which can be attributed to the anion alone. The poor biodegradability values obtained for **5a** does not necessarily mean that the phenyl group on the imidazolium salts cannot act as an oxygen handle, as the position of the phenyl group influences the ability of a compound to mineralize.[11b]

Other attempts to improve biodegradation involved the use of unsaturated groups that might increase the chances of metabolism of the imidazolium cation by redox enzymes. Unsaturated synthetic base fluids are known to undergo microbial biodegradation much faster than their corresponding saturated counterparts under anaerobic conditions.[11b,17] Thus, the allyl and vinyl group were incorporated onto the imidazolium cation (**6** and **7**, respectively). It was rationalized that side chains that are susceptible to oxidation at the carbon attached to the imidazolium nitrogen would afford intermediates which are unstable and not refractory in their nature. Both **6a** and **7a**, however, failed to show good biodegradability, whereas their octyl sulfate counterparts **6b** and **7b** showed biodegradation at 43% (Fig. 1).

We also endeavored to investigate the inclusion of potentially biodegradable anions such as alkylsulfites, lactates, dialkylphosphates, and the anion formed from saccharin, into imidazolium based ILs. ILs containing methylsulfite anions were prepared using a method reported in the literature.[18] Whereas **8a** containing the common dialkylimidazolium cation, 1-butyl-3-methylimidazolium [bmim], showed only 8% biodegradability, the replacement of this cation with one containing an ester side chain, **8b**, increased the percentage biodegradation to 35%.

Lactic acid, a fairly inexpensive, commercially available compound that is produced naturally in catabolic processes was an appealing synthon for an anion in these salts. The lactate ion has been previously incorporated as the anion in ILs that are considered to be greener, since they are produced from a material that is biocompatible and biorenewable.[19] Lactate was also of interest because polylactate is a commercial bioplastic that is also used for making biomaterials used for medical implants. Hence, [bmim][lactate] (**9**) was obtained from the reaction involving [bmim][Cl] with a silver salt of lactic acid and showed only 17% biodegradability after 28 days (Fig. 2). Therefore, **9** cannot be considered to be readily biodegradable.



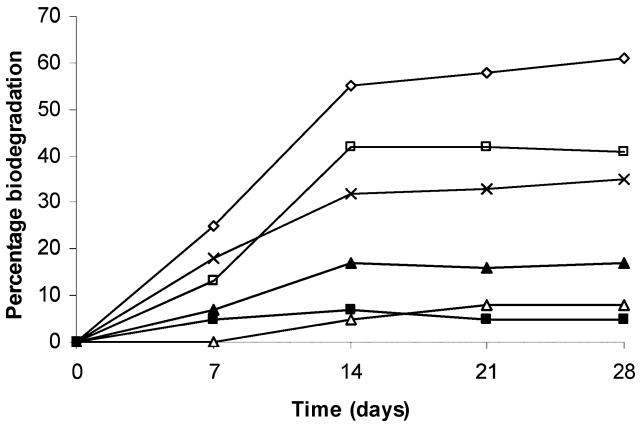


Fig. 2 Effect of anion modifications on percentage biodegradation **8a** (△), **8b** (×), **9** (▲), **10** (■), **11a** (□) and **11b** (◇).

Several natural products such as DNA, ADP, ATP, phospholipids, *etc.* and, perhaps more relevantly, some of the biodegradable detergents, are based on the phosphate group. The most commonly used phosphate containing IL, **10**, was synthesized according to a known protocol,[20] and tested. However, compound **10** also showed poor biodegradability at 5%.

ILs based on saccharin, a well known synthetic non-nutritive sweetener, have been reported in the literature.[21] Saccharin is a common ingredient in food products and therefore has a well established toxicological profile. Its structural features, such as the presence of a phenyl ring with the mixed *N*-acyl-*N*-sulfonyl imide group, makes it an interesting target for evaluation of biodegradability when incorporated into ILs. The [bmim] IL containing the anion produced from saccharin, **11a**, showed biodegradability at 41% (Fig. 2). It is notable that **11a** reached

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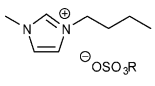
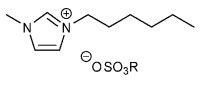
Table 1 Percentage biodegradation of alkyl sulfates based on [bmim] and [hmim] cations after 28 days as determined by the CO_2 headspace test (ISO 14593)



12a R = $(CH_2)_5CH_3$
12b R = $(CH_2)_6CH_3$
12c R = $(CH_2)_7CH_3$
12d R = $(CH_2)_8CH_3$
12e R = $(CH_2)_9CH_3$
12f R = $(CH_2)_{11}CH_3$



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13d R = $(CH_2)_8CH_3$
13e R = $(CH_2)_9CH_3$
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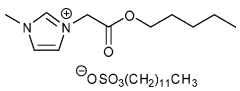

14

Entry	No.	Compound[a]	Biodegradation (%)
1	**12a**	[bmim] [$C_6H_{13}OSO_3$]	34
2	**12b**	[bmim] [$C_7H_{15}OSO_3$]	36
3	**12c**	[bmim] [$C_8H_{17}OSO_3$]	40
4	**12d**	[bmim] [$C_9H_{19}OSO_3$]	47
5	**12e**	[bmim] [$C_{10}H_{21}OSO_3$]	54
6	**12f**	[bmim] [$C_{12}H_{25}OSO_3$]	58
7	**13a**	[hmim] [$C_6H_{13}OSO_3$]	30
8	**13b**	[hmim] [$C_7H_{15}OSO_3$]	33
9	**13c**	[hmim] [$C_8H_{17}OSO_3$]	38
10	**13d**	[hmim] [$C_9H_{19}OSO_3$]	36
11	**13e**	[hmim] [$C_{10}H_{21}OSO_3$]	44
12	**13f**	[hmim] [$C_{12}H_{25}OSO_3$]	49
13	**14**	['ester'-mim] [$C_{12}H_{25}OSO_3$]	72

[a] IL concentration = 40 mg L^{-1}.

its highest level of biodegradability within 14 days of incubation, which has been associated with very high rates of biodegradation of the saccharin anion. The overall biodegradability of the saccharin based IL can be enhanced by incorporating the ester group on the alkyl side chain of the imidazolium ion as in **11b**, which showed biodegradability at 61%. Thus, **11b** containing both an ester linkage in the cation and the saccharin derived anion can be classified as 'readily biodegradable'. The cation modifications thus appear to be necessary to increase the overall biodegradability of saccharin containing ILs to the level where they can be deemed readily biodegradable.

Our previous attempts to search for a biodegradable IL disclosed that the alkyl sulfates are very good anion candidates.[14c,16] However, since the overall biodegradability of ILs appears to be a cumulative contribution from both the cation and the anion, higher biodegradability values are reached in the case of imidazolium based ILs by incorporating the ester group on the side chain in addition to the presence of an alkylsulfate ion.[14a,c] Unfortunately, the ester group on the cation introduces chemical instability, which greatly limits the range of applications for the imidazolium based biodegradable ILs. Therefore, we thought it would be worthwhile to do a thorough investigation on alkyl sulfates based on simple 1,3-dialkylimidazoliums, since they contain typically chemically inert cations, and also offer scope of varying alkyl chain lengths on both the cation as well as the anion.

To investigate how the length of alkyl chain on the alkyl sulfate anion influences the biodegradability of the IL, we first synthesized a series of ILs based on the common imidazolium cation [bmim]. The ILs based on [bmim] with hexyl **12a**, heptyl **12b**, octyl **12c**, nonyl **12d**, decyl **12e** and dodecyl **12f** sulfate were synthesized and tested for biodegradability (Table 1). These ILs were synthesized from [bmim][Cl] and alkyl sulfate ammonium salts obtained by reacting alcohols with sulfamic acid according to a reported procedure.[22] As expected, an increase in the alkyl chain length in the alkyl sulfate ion resulted in an increase in biodegradability. Thus, going from hexyl sulfate **12a** to dodecyl sulfate **12f** the biodegradability increased from 34% to 58%, (Table 1, entries 1 and 6). These findings indicate that the biodegradability of the alkyl sulfate based ILs can be significantly enhanced by increasing the chain length of the alkyl sulfate anion. The recalcitrant nature of the simple 1,3-dialkylimidazolium cation, however, seems to limit the biodegradability values for this series of salts.

We anticipated that an increase in the alkyl chain length on the cation of the 1,3-dialkylimidazolium sulfates would enhance their biodegradability due to increased lipophilicity, which would, in turn, lead to faster absorption of compounds through the cell membranes of the microorganisms present in the test. Thus, the alkyl sulfates based on the 1-hexyl-3-methylimidazolium, [hmim], cation and hexyl **13a**, heptyl **13b**, octyl **13c**, nonyl **13d**, decyl **13e** and dodecyl **13f** sulfates were synthesized and tested for biodegradability. When compared with the corresponding [bmim] based counterparts, the [hmim] based alkyl sulfates showed slightly lower values of biodegradability. With an increase in the alkyl chain length from C_6 to C_{12} on the alkyl sulfate anion, the biodegradability increased from 30% to 49% (Table 1, entries 7–12).

We initially thought that the slightly lower biodegradability observed for the [hmim] series (relative to [bmim]) may have been a result of the longer alkyl chain imparting a biocidal effect. Previous studies have found that the antimicrobial activity of dialkylimidazolium ILs is associated with the cation, and that potency increases with alkyl chain length.[23] In order to assess the potential toxicity of the 1,3-dialkylimidazolium cations to the aerobic microorganisms responsible for biodegradation, solutions containing a mixture of the test substance and a reference compound (sodium *n*-dodecyl sulfate, SDS) were tested (Table 2, entries 1–3). Biodegradation percentages for the mixtures of dialkylimidazolium octylsulfates and SDS were calculated based on the theoretical inorganic carbon (IC) yield from the anion and SDS only, as the imidazolium cation was found to undergo negligible mineralisation in this test.[14c] In both cases, similar rates were observed for the mixtures (IL + SDS) and the reference substance SDS alone. This suggests that neither the [bmim] or [hmim] cations are inhibitory to the inoculum at the concentration used in the biodegradation tests. Furthermore,

Table 2 Percentage biodegradation of **12c** and **13c** at different concentrations and in combination with the reference substance SDS

Entry	Compound[a]	Concentration/ mgC L^{-1}	Biodegradation (%)[a]
1	SDS	20	82
2	[bmim][$C_8H_{17}OSO_3$] + SDS	20 + 20	85
3	[hmim][$C_8H_{17}OSO_3$] + SDS	20 + 20	81
4	[bmim][$C_8H_{17}OSO_3$]	6	40
5	[bmim][$C_8H_{17}OSO_3$]	11	45
6	[bmim][$C_8H_{17}OSO_3$]	20	42
7	[hmim][$C_8H_{17}OSO_3$]	6	38
8	[hmim][$C_8H_{17}OSO_3$]	11	40
9	[hmim][$C_8H_{17}OSO_3$]	20	40

[a] Percent biodegradation after 28 days as determined by the CO_2 headspace test (ISO 14593).

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the dialkylimidazolium octylsulfates **12c** and **13c** were each tested at different concentrations (6, 11 and 20 mgC L^{-1}) and were found to undergo similar levels of biodegradation in each case (Table 2, entries 4–6 and 7–9). This result also supports the conclusion that these dialkylimidazolium cations are not inhibiting the inoculum. Alternatively, the slightly higher values of biodegradation for the [bmim] based alkyl sulfates, when compared to the corresponding [hmim] alkyl sulfates, may be attributed to the larger ratio of mineralized organic carbon (alkylsulfate anion) to total organic carbon content (alkylsulfate anion + 1,3-dialkylimidazolium cation).

Conclusion

In conclusion, functionalization of the *N*-substituent of imidazolium based ILs appears to impart a degree of biodegradability. When paired with alkylsulfate ions, biodegradability of these salts increases appreciably. This is consistent with earlier studies performed by our group.[14] Amongst the anions tested, lactate and that derived from saccharin seem to possess good mineralization abilities. The saccharin based ILs offer good biodegradability values with very high initial biodegradation. Their biodegradability values are as high as their octyl sulfate based counterparts, making them a good anion alternative. The biodegradability of the 1,3-disubstituted imidazolium alkyl sulfates increases with an increase in the alkyl chain length on the alkyl sulfate, but decreases slightly with an increase in the alkyl chain length on the imidazolium cation. Accordingly, the percent biodegradation found after 21 days reflects the proportions of the refractory imidazolium cation and the biodegradable alkylsulfate anion in the IL, when expressed as a percentage of the theoretical amount of inorganic carbon (ThIC).

Experimental

^{1}H and ^{13}C NMR spectra of the purified products were recorded in $CDCl_3$ (Cambridge Isotope Laboratories Inc., 99.8% D) or DMSO-d_6 (Cambridge Isotope Laboratories Inc., 99.9% D) on a Bruker Avance DPX 300 spectrometer at 300 and 75.4 MHz, respectively. Low resolution mass spectra using electrospray ionisation (MS-ESI) were obtained using a Micromass Platform II instrument.

Synthesis of ammonium octylsulfate[22]

1-Octanol (3.00 g, 15.7 mL, 100 mmol) and sulfamic acid (9.70 g, 100 mmol) were heated at 110 °C for 24 h in a moisture guarded assembly. The reaction mixture was allowed to cool down to room temperature, when it solidified. The fused waxy mass was treated with hexane (500 mL) and stirred vigorously for 1 h after mechanically crushing the lumpy solid. The filtration of hexanes yielded the crude product which was washed with hexane (3 × 50 mL) and dried under reduced pressure. The crude product was stirred with dichloromethane (200 mL) for 1 h, followed by precipitation with hexane (800 mL) to yield the pure product. The product was filtered, washed with hexane (3 × 50 mL) and dried under reduced pressure. Yield 69%. ^{1}H NMR (DMSO-d_6): δ 0.83–0.87 (t, J = 6.6 Hz, 3H), 1.24 (br s, 10H), 1.44–1.51 (m, 2H), 3.67–3.71 (t, J = 6.6 Hz, 2H), 6.93–7.26 (t, J = 49.2 Hz, 4H). ^{13}C NMR (DMSO-d_6): δ 14.0, 22.2, 25.6, 28.8, 28.9, 29.2, 31.4, 66.0. MS (ESI, 20 eV): m/z 209.3 $[C_8H_{17}OSO_3]^-$.

General method for the synthesis of the dialkylimidazolium halides 1a, 5a and 6a

Alkyl halide (40.0 mmol) was added to the solution of 1-alkylimidazole (33.3 mmol) in toluene (20 mL) at 0 °C. The reaction mixture was maintained under a nitrogen atmosphere. The stirring was continued at room temperature for 1 h under nitrogen and then heated at 70 °C for 24 h. The work-up and isolation procedures were the same as with method 1 above. These quaternary salts/ILs, being hygroscopic, were handled under nitrogen at each stage of synthesis and purification.

1-Methyl-3-(pentoxycarbonylmethyl)imidazolium bromide (1a)[14c]. Yield 97%. ^{1}H NMR (DMSO-d_6): δ 0.86–0.90 (t, J = 6.9 Hz, 3H), 1.26–1.34 (m, 4H), 1.57–1.66 (m, 2H), 3.92 (s, 3H), 4.13–4.18 (t, J = 6.6 Hz, 2H), 5.26 (s, 2H), 7.73–7.74 (m, 2H), 9.11 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 13.7, 21.6, 27.3, 27.5, 35.9, 49.4, 65.6, 123.3, 123.6, 137.6, 166.8. MS (ESI, 20 eV): m/z 211.1 $[M–Br^-]^+$; MS (ESI, 20 eV): m/z 78.9 and 80.9 $[Br]^-$.

3-Benzyl-1-methylimidazolium bromide (5a). Yield 97%. ^{1}H NMR (DMSO-d_6): δ 3.89 (s, 3H), 5.58 (s, 2H), 7.30–7.34 (m, 3H), 7.51–7.54 (m, 2H), 7.86–7.87 (m, 1H), 7.98–7.99 (m, 1H), 9.66 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 35.9, 51.4, 122.0, 123.7, 128.3, 128.5, 128.7, 134.8, 136.4. MS (ESI, 20 eV): m/z 173.1 $[M–Br^-]^+$; MS (ESI, 20 eV): m/z 78.9 and 80.8 $[Br]^-$.

3-Allyl-1-methylimidazolium bromide (6a). Yield 95%. ^{1}H NMR (DMSO-d_6): δ 3.90 (s, 3H), 4.93–4.95 (d, J = 6.0 Hz, 2H), 5.26–5.27 (m, 1H), 5.30–5.32 (m, 1H), 5.95–6.08 (m, 1H), 7.87 (s, 2H) 9.45–9.46 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 35.8, 50.4, 120.1, 122.1, 123.5, 131.6, 136.4. MS (ESI, 20 eV): m/z 123.1 $[M–Br^-]^+$; MS (ESI, 20 eV): m/z 78.9 and 80.8 $[Br]^-$.

General method for the synthesis of the dialkylimidazolium halides 2, 3a and 7a

A mixture of 1-alkylimidazole (33.3 mmol) and alkyl halide (40.0 mmol) in toluene (20 mL) was heated at 110 °C for 24 h under a nitrogen atmosphere. The completion of reaction was marked by the separation of either dense IL or salt. The product was isolated by decanting toluene to remove any unreacted starting materials and solvent. Subsequently, the IL was washed with diethyl ether (4 × 20 mL) and the ether layer was separated from the IL/salt by decantation. In some cases, the ether washings resulted in the formation of a solid. The solid was purified by dissolving in acetonitrile (10–20 mL) and precipitation with diethyl ether (60–70 mL). In each case, the IL or salt was finally dried under reduced pressure to get rid of the volatile organic compounds.

3-(2-Hydroxyethyl)-1-methylimidazolium bromide (2). Yield 98%. ^{1}H NMR (DMSO-d_6): δ 3.68–3.73 (m, 2H), 3.88 (s, 3H), 4.23–4.26 (t, J = 5.1 Hz, 2H), 5.11–5.14 (t, J = 5.25 Hz, 1H), 7.76–7.79 (m, 2H), 9.24 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 35.8, 51.4, 59.1, 122.5, 123.1, 136.6. MS (ESI, 20 eV): m/z 127.0 $[M–Br^-]^+$; MS (ESI, 100 eV): m/z 78.8 and 80.8 $[Br]^-$.

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3-(4-Acetoxybutyl)-1-methylimidazolium iodide (3a). Yield 96%. ^{1}H NMR (DMSO-d_6): δ 1.48–1.58 (m, 2H), 1.78–1.88 (m, 2H), 1.97 (s, 3H), 3.86 (s, 3H), 3.95–3.99 (t, J = 6.5 Hz, 2H), 4.20–4.25 (t, J = 7.2 Hz, 2H), 7.75 (s, 1H), 7.83–7.84 (m, 1H), 9.22 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 20.8, 24.7, 26.1, 36.0, 48.3, 63.0, 122.1, 123.4, 136.4, 170.3. MS (ESI, 20 eV): m/z 197.1 [M-I$^-$]$^+$; MS (ESI, 70 eV): m/z 127.0 [I]$^-$.

1-Butyl-3-vinylimidazolium iodide (7a). Yield 100%. ^{1}H NMR (DMSO-d_6): δ 0.85–0.90 (t, J = 7.4 Hz, 3H), 1.21–1.33 (m, 2H), 1.76–1.86 (m, 2H), 4.20–4.25 (t, J = 7.4 Hz, 2H), 5.40–5.44 (dd, J = 2.4, 8.7 Hz, 1H), 5.94–6.00 (dd, J = 2.4, 15.6 Hz, 1H), 7.26–7.34 (dd, J = 8.7, 15.6 Hz, 1H), 7.97–7.98 (m, 1H), 8.21–8.23 (m, 1H), 9.60–9.61 (m, 1H). ^{13}C NMR (DMSO-d_6): δ 13.2, 18.6, 30.9, 48.9, 108.7, 119.1, 123.1, 128.6, 135.0. MS (ESI, 20 eV): m/z 151.2 [M–I$^-$]$^+$; MS (ESI, 70 eV): m/z 127.0 [I]$^-$.

General method for the synthesis of the dialkylimidazolium octylsulfates 1b, 3b, 5b, 6b, 7b and 14

The quaternary 1,3-dialkylimidazolium halide (2 mmol) was dissolved in water to obtain a clear solution. The aqueous solution of quaternary halide was treated with the aqueous solution of ammonium octyl sulfate (2 mmol in 10 mL of water) and the resulting mixture was stirred for 10 min. The product was isolated by solvent extraction using dichloromethane (3 × 10 mL). The extracts were dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to yield the required product.

1-Methyl-3-(pentoxycarbonylmethyl)imidazolium octylsulfate (1b).[14c] Yield 98%. ^{1}H NMR (DMSO-d_6): δ 0.84–0.90 (m, 6H), 1.25–1.34 (m, 14H), 1.45–1.50 (m, 2H), 1.60–1.64 (m, 2H), 3.64–3.69 (t, J = 7.4 Hz, 2H), 3.91 (s, 3H), 4.13–4.18 (t, J = 6.6 Hz, 2H), 5.24 (s, 2H), 7.72 (s, 2H), 9.07 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 13.7, 13.8, 21.6, 22.0, 25.5, 27.3, 27.6, 28.6, 28.7, 29.0, 31.2, 35.9, 49.4, 65.4, 65.7, 123.3, 123.7, 137.7, 166.8. MS (ESI, 20 eV): m/z 211.2 [M–$C_8H_{17}OSO_3^-$]$^+$; MS (ESI, 20 eV): m/z 209.1 [$C_8H_{17}OSO_3$]$^-$.

3-(4-Acetoxybutyl)-1-methylimidazolium octylsulfate (3b). Yield 94%. ^{1}H NMR (DMSO-d_6): δ 0.84–0.88 (t, J = 6.6 Hz, 3H), 1.25 (br s, 10H), 1.45–1.61 (m, 4H), 1.79–1.89 (m, 2H), 2.00 (s, 3H), 3.64–3.69 (t, J = 6.8 Hz, 2H), 3.85 (s, 3H), 4.00–4.04 (t, J = 6.6 Hz, 2H), 4.17–4.21 (t, J = 7.2 Hz, 2H), 7.70 (s, 1H), 7.76 (s, 1H), 9.09 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 13.8, 20.6, 22.0, 24.7, 25.5, 26.1, 28.6, 28.7, 29.0, 31.2, 35.7, 48.3, 63.0, 65.4, 122.2, 123.6, 136.6, 170.3. MS (ESI, 20 eV): m/z 197.1 [M-$C_8H_{17}OSO_3^-$]$^+$; MS (ESI, 20 eV): m/z 209.0 [$C_8H_{17}OSO_3$]$^-$.

3-Benzyl-1-methylimidazolium octylsulfate (5b). Yield 88%. ^{1}H NMR (DMSO-d_6): δ 0.84–0.88 (t, J = 6.2 Hz, 3H), 1.25 (br s, 10H), 1.45–1.50 (m, 2H), 3.65–3.69 (t, J = 6.6 Hz, 2H), 3.86 (s, 3H), 5.42 (s, 2H), 7.39–7.43 (m, 5H), 7.70–7.71 (m, 1H), 7.77–7.78 (m, 1H) 9.20 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 13.9, 22.0, 25.5, 28.6, 28.7, 29.0, 31.2, 35.8, 51.8, 65.4, 122.3, 124.0, 128.3, 128.7, 128.9, 134.8, 136.7. MS (ESI, 20 eV): m/z 173.2 [M–$C_8H_{17}OSO_3^-$]$^+$; MS (ESI, 20 eV): m/z 209.1 [$C_8H_{17}OSO_3$]$^-$.

3-Allyl-1-methylimidazolium octylsulfate (6b). Yield 91%. ^{1}H NMR (DMSO-d_6): δ 0.84–0.88 (t, J = 6.3 Hz, 3H), 1.25 (br s, 10H), 1.45–1.50 (m, 2H), 3.64–3.69 (t, J = 6.6 Hz, 2H), 3.86 (s, 3H), 4.83–4.85 (d, J = 6.0 Hz, 2H), 5.27–5.39 (m, 2H), 5.98–6.11 (m, 1H), 7.70–7.72 (m, 2H) 9.09 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 13.8, 22.0, 25.5, 28.6, 28.7, 29.0, 31.2, 35.7, 50.7, 65.5, 120.1, 122.3, 123.7, 131.7, 136.6. MS (ESI, 20 eV): m/z 123.0 [M–$C_8H_{17}OSO_3^-$]$^+$; MS (ESI, 20 eV): m/z 209.2 [$C_8H_{17}OSO_3$]$^-$.

1-Butyl-3-vinylimidazolium octylsulfate (7b). Yield 87%. ^{1}H NMR (DMSO-d_6): δ 0.83–0.94 (m, 6H), 1.24–1.36 (m, 12H), 1.43–1.50 (m, 2H), 1.76–1.86 (m, 2H), 3.66–3.70 (t, J = 6.9 Hz, 2H), 4.18–4.23 (t, J = 7.2 Hz, 2H), 5.40–5.44 (dd, J = 2.4, 9.0 Hz, 1H), 5.92–5.98 (dd, J = 2.1, 15.6 Hz, 1H), 7.24–7.32 (dd, J = 8.7, 15.6 Hz, 1H), 7.92–7.93 (m, 1H), 8.18–8.19 (m, 1H), 9.48 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 13.2, 13.8, 18.7, 22.0, 25.5, 28.6, 28.7, 29.0, 31.0, 31.2, 48.9, 65.5, 108.6, 119.1, 123.2, 128.8, 135.3. MS (ESI, 20 eV): m/z 151.2 [M–$C_8H_{17}OSO_3^-$]$^+$; MS (ESI, 70 eV): m/z 209.1 [$C_8H_{17}OSO_3$]$^-$.

1-Methyl-3-(pentoxycarbonylmethyl)imidazolium dodecylsulfate (14). Yield 95%. ^{1}H NMR (DMSO-d_6): δ 0.83–0.91 (m, 6H), 1.25–1.33 (m, 22H), 1.45–1.49 (m, 2H), 1.60–1.64 (m, 2H), 3.64–3.69 (t, J = 6.8 Hz, 2H), 3.91 (s, 3H), 4.13–4.18 (t, J = 6.6 Hz, 2H), 5.24 (s, 2H), 7.72 (s, 2H), 9.07 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 13.7, 13.8, 21.6, 22.0, 25.5, 27.3, 27.6, 28.6, 28.7, 28.9, 29.0, 29.0, 31.2, 35.9, 49.4, 65.4, 65.6, 123.3, 123.7, 137.7, 166.8. MS (ESI, 20 eV): m/z 211.1 [M–$C_{12}H_{25}OSO_3^-$]$^+$; MS (ESI, 20 eV): m/z 265.2 [$C_{12}H_{25}OSO_3$]$^-$.

4-(1-Methylimidazolium-3-yl)butane-1-sulfonate (4). Compound **4** was prepared using literature methodology;[24] yield 100%. ^{1}H NMR (D_2O): 1.80–1.90 (m, 2H), 2.08–2.18 (m, 2H), 3.02–3.07 (t, J = 7.7 Hz, 2H), 4.00 (s, 3H), 4.33–4.38 (t, J = 7.1 Hz, 2H), 7.54–7.55 (m, 1H), 7.60–7.61 (m, 1H), 8.83 (s, 1H). ^{13}C NMR (D_2O): δ 21.1, 28.2, 35.8, 49.0, 50.2, 122.3, 123.8, 136.1. MS (ESI): m/z 219.1 (100%, [$C_8H_{14}N_2O_3S$ + 1]$^+$).

General method for the synthesis of the dialkylimidazolium methanesulfonates 8a–b[18]

The mixture of 1-alkylimidazole (33.3 mmol) and butylmethanesulfonate (36.6 equiv.) was refluxed for 24 h in toluene (20 mL) maintaining an inert atmosphere. The IL separates from the reaction mixture. The toluene layer was separated from the IL by decantation. The separated IL was washed with diethyl ether (3 × 20 mL) followed by drying/removal of volatile components by evaporation under reduced pressure.

3-Butyl-1-methylimidazolium methanesulfonate (8a). Yield 97%. ^{1}H NMR (DMSO-d_6): δ 0.87–0.92 (t, J = 7.4 Hz, 3H), 1.22–1.30 (m, 2H), 1.71–1.81 (m, 2H), 2.31–2.32 (m, 3H), 3.85 (s, 3H), 4.14–4.19 (t, J = 7.1 Hz, 2H), 7.69–7.70 (m, 1H), 7.76–7.77 (m, 1H), 9.14 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 13.2, 18.7, 31.3, 35.6, 39.7, 48.4, 122.3, 123.6, 136.7. MS (ESI, 20 eV): m/z 139.2 [M–$CH_3SO_3^-$]$^+$; MS (ESI, 20 eV): m/z 95.0 [CH_3SO_3]$^-$.

1-Methyl-3-(2-oxo-2-(pentyloxy)ethyl)imidazolium methanesulfonate (8b). Yield 88%. ^{1}H NMR (DMSO-d_6): δ 0.85–0.93 (m, 6H), 1.22–1.31 (m, 6H), 1.58–1.63 (m, 2H), 1.75–1.80 (m, 2H), 2.30–2.31 (m, 3H), 4.13–4.17 (t, J = 6.6 Hz, 2H), 4.22–4.26 (t, J = 7.1 Hz, 2H), 5.24 (s, 2H), 7.74–7.75 (m, 1H), 7.82–7.83 (s, 1H), 9.16–9.17 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 13.2, 13.7, 18.7, 21.6, 27.3, 27.6, 31.3, 39.7, 48.7, 49.5, 65.7, 122.1, 123.9,

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137.3, 166.8. MS (ESI, 20 eV): m/z 253.4 $[M–CH_3SO_3^-]^+$; MS (ESI, 20 eV): m/z 95.0 $[CH_3SO_3]^-$.

3-Butyl-1-methylimidazolium lactate (9). To the solution of [bmim][Cl] (2.44 mmol) in water (10 mL) was added the solution of silver lactate (2.93 mmol) in water (10 mL). The reaction mixture was stirred for 10 min at room temperature in the dark. The reaction mixture was freeze dried to yield the IL containing silver chloride. The IL was extracted in chloroform. The extract was filtered to remove the insoluble silver chloride, dried over anhydrous magnesium sulfate and finally evaporated at reduced pressure to yield **9**: yield 91%. ^{1}H NMR (DMSO-d_6): δ 0.87–0.91 (t, J = 7.4 Hz, 3H), 1.04–1.08 (d, J = 5.6 Hz, 3H), 1.22–1.29 (m, 2H), 1.71–1.81 (m, 2H), 3.45–3.52 (q, J = 7.1 Hz, 1H), 3.86 (s, 3H), 4.15–4.20 (t, J = 7.2 Hz, 2H), 7.73–7.74 (m, 1H), 7.80–7.81 (m, 1H), 9.42 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 13.2, 18.7, 21.5, 31.3, 35.6, 48.4, 67.00, 122.2, 123.6, 136.9, 176.9. MS (ESI, 20 eV): m/z 139.1 $[M–C_3H_5O_3^-]^+$; MS (ESI, 20 eV): m/z 89.1 $[C_3H_5O_3]^-$.

3-Butyl-1-methylimidazolium dibutylphosphate (10)[20]

The mixture of 1-methylimidazole (33.3 mmol) and tributyl phosphate (33.3 mmol) were heated in a moisture guarded assembly at 150 °C for 24 h. The resulting brown viscous liquid was washed with diethyl ether (3 × 20 mL). The resultant IL was first heated at reduced pressure by rotary evaporation followed by removal of all volatile residues under reduced pressure over 24 h under vacuum; yield 92%. ^{1}H NMR ($CDCl_3$): δ 0.84–0.96 (m, 9H), 1.29–1.43 (m, 6H), 1.54–1.63 (m, 4H), 1.79–1.89 (m, 2H), 3.82–3.89 (m, 4H), 4.04 (s, 3H), 4.25–4.30 (t, J = 7.4 Hz, 2H), 7.20–7.21 (m, 1H), 7.31–7.32 (m, 1H), 10.48 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 13.4, 13.8, 19.1, 19.5, 32.2, 33.0, 33.1, 36.4, 49.6, 64.9, 65.0, 121.7, 123.6, 139.2. MS (ESI, 20 eV): m/z 139.2 $[M–C_8H_{18}O_4P^-]^+$; MS (ESI, 20 eV): m/z 209.2 $[C_8H_{18}O_4P]^-$.

General method for the synthesis of the dialkylimidazolium saccharinates 11a–b

The syntheses of **11a** and **11b** was achieved by slightly modifying the procedure reported earlier, in that a two fold excess of sodium saccharin was used which bypassed the purification step that involves column chromatography.[21] Acetone (100 mL) was added to the mixture of 1,3-dialkylimidazolium chloride (33.3 mmol) and finely crushed saccharin sodium salt (66.6 equiv.). The resultant biphasic mixture was stirred vigorously at room temperature for 24 h. After completion of the metathesis, the reaction mixture was filtered and the filtrate was evaporated under reduced pressure to yield the saccharin based ILs.

3-Butyl-1-methylimidazolium saccharinate (11a). Yield 88%. ^{1}H NMR ($CDCl_3$): δ 0.88–0.93 (t, J = 7.4 Hz, 3H), 1.25–1.40 (m, 2H), 1.79–1.89 (m, 2H), 4.07 (s, 3H), 4.26–4.31 (t, J = 7.4 Hz, 2H), 7.25–7.27 (m, 1H), 7.32–7.33 (m, 1H), 7.55–7.59 (m, 2H), 7.74–7.81 (m, 2H), 10.00 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 13.3, 19.3, 32.0, 36.4, 49.6, 119.5, 122.1, 123.1, 123.6, 131.3, 132.0, 134.8, 137.2, 144.7, 170.1. MS (ESI, 20 eV): m/z 139.1 $[M–C_7H_4NO_3S^-]^+$; MS (ESI, 20 eV): m/z 182.1 $[C_7H_4NO_3S]^-$.

1-Methyl-3-(pentoxycarbonylmethyl)imidazolium saccharinate (11b). Yield 91%. ^{1}H NMR ($CDCl_3$): δ 0.85–0.91 (t, J = 8.6 Hz, 3H), 1.26–1.33 (m, 4H), 1.58–1.67 (m, 2H), 4.05 (s, 3H), 4.14–4.18 (t, J = 6.9 Hz, 2H), 5.34 (s, 2H), 7.33–7.34 (m, 1H), 7.43–7.45 (m, 1H), 7.55–7.59 (m, 2H), 7.71–7.79 (m, 2H), 9.94 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 14.0, 22.3, 27.9, 28.1, 36.7, 50.2, 67.0, 119.9, 123.2, 123.4, 123.8, 131.7, 132.2, 134.7, 139.2 144.6, 166.6, 170.2. MS (ESI, 20 eV): m/z 211.4 $[M–C_7H_4NO_3S^-]^+$; MS (ESI, 20 eV): m/z 182.3 $[C_7H_4NO_3S]^-$.

General method for the synthesis of dialkylimidazolium alkylsufates (12a–f and 13a–f)[25]

The primary alcohol (26.4 mmol) and sulfamic acid (26.4 mmol) were heated at 85 °C for 24 h in a moisture guarded assembly. The reaction mixture was allowed to cool down to room temperature, during which it might solidify. The reaction mass was extracted into water (100 mL) and [bmim][Cl] or [hmim][Cl] (20.24 mmol) was added to the solution and the mixture stirred for 10 min. The resultant aqueous solution was washed with diethyl ether (3 × 50 mL), and the product was finally extracted into dichloromethane (3 × 50 mL). The dichloromethane extracts were dried over anhydrous $MgSO_4$, and concentrated by evaporation of the solvent under reduced pressure. The resulting oil was stirred at reduced pressure at 60 °C for 4 h.

3-Butyl-1-methylimidazolium hexylsulfate (12a). Yield 37%. ^{1}H NMR ($CDCl_3$): δ 0.64–0.77 (m, 6H), 1.07–1.30 (m, 8H), 1.39–1.50 (m, 2H), 1.62–1.74 (m, 2H), 3.68–3.83 (m, 5H), 4.04–4.10 (t, J = 7.2 Hz, 2H), 7.36–7.38 (m, 1H), 7.44–7.46 (m, 1H), 9.27 (s, 1H). ^{13}C NMR ($CDCl_3$): 13.0, 13.6, 19.0, 22.1, 25.1, 29.1, 31.1, 31.7, 35.9, 49.2, 67.2, 122.1, 123.6, 136.9. MS (ESI, 20 eV): m/z 139.6 $[M–C_6H_{13}OSO_3^-]^+$; MS (ESI, 20 eV): m/z 181.1 $[C_6H_{13}OSO_3]^-$.

3-Butyl-1-methylimidazolium heptylsulfate (12b). Yield 36%. ^{1}H NMR ($CDCl_3$): δ 0.61–0.73 (m, 6H), 0.95–1.23 (m, 10H), 1.32–1.50 (m, 2H), 1.60–1.73 (m, 2H), 3.73–3.81 (m, 5H), 4.00–4.06 (t, J = 7.2 Hz, 2H), 7.34–7.36 (m, 1H), 7.41–7.42 (m, 1H), 9.21 (s, 1H). ^{13}C NMR ($CDCl_3$): 12.9, 13.5, 18.9, 22.0, 25.3, 28.5, 29.1, 31.3, 31.6, 35.7, 49.1, 67.0, 122.0, 123.5, 136.7. MS (ESI, 20 eV): m/z 139.2 $[M–C_7H_{15}OSO_3^-]^+$; MS (ESI, 20 eV): m/z 195.4 $[C_7H_{15}OSO_3]^-$.

3-Butyl-1-methylimidazolium octylsulfate (12c). Yield 83%. ^{1}H NMR (DMSO-d_6): δ 0.84–0.93 (m, 6H), 1.23–1.30 (m, 12H), 1.45–1.50 (m, 2H), 1.74–1.79 (m, 2H), 3.65–3.70 (t, J = 6.6 Hz, 2H), 3.85 (s, 3H), 4.14–4.19 (t, J = 7.2 Hz, 2H), 7.69–7.70 (m, 1H), 7.76–7.77 (m, 1H), 9.10 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 13.2, 13.8, 18.7, 22.0, 25.5, 28.6, 28.7, 29.0, 31.2, 31.3, 35.7, 48.4, 65.4, 122.2, 123.6, 136.5. MS (ESI, 20 eV): m/z 139.1 $[M–C_8H_{17}OSO_3^-]^+$; MS (ESI, 20 eV): m/z 209.3 $[C_8H_{17}OSO_3]^-$.

3-Butyl-1-methylimidazolium nonylsulfate (12d). Yield 83%. ^{1}H NMR ($CDCl_3$): δ 0.82–0.96 (m, 6H), 1.27–1.41 (m, 14H), 1.58–1.69 (m, 2H), 1.78–1.90 (m, 2H), 3.97–4.03 (m, 5H), 4.18–4.24 (t, J = 7.2 Hz, 2H), 7.37–7.39 (m, 1H), 7.47–7.49 (m, 1H), 9.42 (s, 1H). ^{13}C NMR ($CDCl_3$): 13.4, 14.1, 19.5, 22.7, 26.0, 29.3, 29.4, 29.6, 29.7, 31.9, 32.1, 36.4, 49.8, 67.9, 122.2, 123.9, 137.5. MS (ESI, 20 eV): m/z 139.2 $[M–C_9H_{19}OSO_3^-]^+$; MS (ESI, 20 eV): m/z 223.4 $[C_9H_{19}OSO_3]^-$.

3-Butyl-1-methylimidazolium decylsulfate (12e). Yield 19%. ^{1}H NMR ($CDCl_3$): δ 0.81–0.95 (m, 6H), 1.21–1.40 (m, 16H),

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1.57–1.65 (m, 2H), 1.81–1.89 (m, 2H), 3.96–4.01 (m, 5H), 4.18–4.24 (t, $J = 7.2$ Hz, 2H), 7.39–7.40 (m, 1H), 7.49–7.50 (m, 1H), 9.47 (s, 1H). ^{13}C NMR ($CDCl_3$): 13.3, 14.0, 19.4, 22.6, 25.8, 29.2, 29.3, 29.5, 29.5, 29.6, 31.8, 32.0, 36.3, 49.7, 67.6, 122.3, 123.9, 137.4. MS (ESI, 20 eV): m/z 139.2 [M–$C_9H_{19}OSO_3^-$]$^+$; MS (ESI, 20 eV): m/z 237.4 [$C_{10}H_{21}OSO_3$]$^-$.

3-Butyl-1-methylimidazolium dodecylsulfate (12f). Yield 95%. ^{1}H NMR (DMSO-d_6): δ 0.83–0.93 (m, 6H), 1.21–1.30 (m, 20H), 1.45–1.49 (m, 2H), 1.74–1.79 (m, 2H), 3.65–3.69 (t, $J = 6.6$ Hz, 2H), 3.85 (s, 3H), 4.14–4.18 (t, $J = 7.2$ Hz, 2H), 7.69 (s, 1H), 7.76 (s, 1H), 9.10 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 13.3, 14.0, 19.3, 22.6, 25.8, 29.3, 29.3, 29.5, 29.5, 29.6, 29.6, 29.6, 31.8, 32.0, 36.2, 49.6, 67.6, 122.2, 123.9, 137.3. MS (ESI, 20 eV): m/z 139.1 [M–$C_{12}H_{25}OSO_3^-$]$^+$; MS (ESI, 20 eV): m/z 265.2 [$C_{12}H_{25}OSO_3$]$^-$.

3-Hexyl-1-methylimidazolium hexylsulfate (13a). Yield 46%. ^{1}H NMR ($CDCl_3$): δ 0.84–0.90 (m, 6H), 1.27–1.39 (m, 12H), 1.59–1.69 (m, 2H), 1.83–1.92 (m, 2H), 3.98–4.06 (m, 5H), 4.22–4.28 (t, $J = 7.5$ Hz, 2H), 7.52–7.55 (m, 1H), 7.65–7.67 (m, 1H), 9.50 (s, 1H). ^{13}C NMR ($CDCl_3$): 13.9, 14.0, 22.4, 22.6, 25.6, 25.9, 29.5, 30.2, 31.1, 31.5, 36.3, 49.9, 67.5, 122.5, 124.1, 137.1. MS (ESI, 20 eV): m/z 167.1 [M–$C_6H_{13}OSO_3^-$]$^+$; MS (ESI, 20 eV): m/z 180.8 [$C_6H_{13}OSO_3$]$^-$.

3-Hexyl-1-methylimidazolium heptylsulfate (13b). Yield 74%. ^{1}H NMR ($CDCl_3$): δ 0.84–0.90 (m, 6H), 1.26–1.41 (m, 14H), 1.62–1.69 (m, 2H), 1.85–1.91 (m, 2H), 3.98–4.05 (m, 5H), 4.21–4.28 (t, $J = 7.3$ Hz, 2H), 7.51–7.53 (m, 1H), 7.64–7.66 (m, 1H), 9.46 (s, 1H). ^{13}C NMR ($CDCl_3$): 13.9, 14.0, 22.4, 22.6, 25.9, 29.0, 29.2, 29.6, 30.2, 31.1, 31.7, 36.3, 49.9, 67.6, 122.4, 124.1, 137.2. MS (ESI, 20 eV): m/z 167.1 [M–$C_7H_{15}OSO_3^-$]$^+$; MS (ESI, 20 eV): m/z 194.8 [$C_7H_{15}OSO_3$]$^-$.

3-Hexyl-1-methylimidazolium octylsulfate (13c). Yield 93%. ^{1}H NMR ($CDCl_3$): δ 0.83–0.90 (m, 6H), 1.21–1.41 (m, 16H), 1.62–1.69 (m, 2H), 1.83–1.90 (m, 2H), 3.99–4.06 (m, 5H), 4.20–4.26 (t, $J = 7.4$ Hz, 2H), 7.39–7.41 (m, 1H), 7.53–7.55 (m, 1H), 9.47 (s, 1H). ^{13}C NMR ($CDCl_3$): 13.9, 14.1, 22.4, 22.6, 25.9, 29.3, 29.4, 29.5, 29.6, 30.2, 31.1, 31.8, 36.3, 49.9, 67.6, 122.3, 124.0, 137.3. MS (ESI, 20 eV): m/z 167.1 [M–$C_8H_{17}OSO_3^-$]$^+$; MS (ESI, 20 eV): m/z 208.8 [$C_8H_{17}OSO_3$]$^-$.

3-Hexyl-1-methylimidazolium nonylsulfate (13d). Yield 80%. ^{1}H NMR ($CDCl_3$): δ 0.84–0.90 (m, 6H), 1.14–1.40 (m, 18H), 1.59–1.69 (m, 2H), 1.82–1.90 (m, 2H), 3.98–4.06 (m, 5H), 4.20–4.27 (t, $J = 7.3$ Hz, 2H), 7.47–7.49 (m, 1H), 7.61–7.62 (m, 1H), 9.46 (s, 1H). ^{13}C NMR ($CDCl_3$): 14.0, 14.1, 22.4, 22.7, 25.9, 29.1, 29.3, 29.4, 29.5, 29.6, 30.2, 31.1, 31.9, 36.3, 49.9, 67.7, 122.3, 124.0, 137.3. MS (ESI, 20 eV): m/z 167.1 [M–$C_9H_{19}OSO_3^-$]$^+$; MS (ESI, 20 eV): m/z 222.8 [$C_9H_{19}OSO_3$]$^-$.

3-Hexyl-1-methylimidazolium decyl sulfate (13e). Yield 93%. ^{1}H NMR ($CDCl_3$): δ 0.84–0.90 (m, 6H), 1.21–1.45 (m, 20H), 1.62–1.69 (m, 2H), 1.83–1.91 (m, 2H), 3.93–4.06 (m, 5H), 4.20–4.26 (t, $J = 7.5$ Hz, 2H), 7.44–7.46 (m, 1H), 7.57–7.60 (m, 1H), 9.50 (s, 1H). ^{13}C NMR ($CDCl_3$): 13.9, 14.1, 22.4, 22.7, 25.90, 25.93, 29.3, 29.4, 29.5, 29.6, 29.7, 30.2, 31.1, 31.9, 36.4, 50.0, 67.7, 122.2, 124.0, 137.4. MS (ESI, 20 eV): m/z 167.1 [M–$C_{10}H_{21}OSO_3^-$]$^+$; MS (ESI, 20 eV): m/z 236.9 [$C_{10}H_{21}OSO_3$]$^-$.

3-Hexyl-1-methylimidazolium dodecylsulfate (13f). Yield 81%. ^{1}H NMR ($CDCl_3$): δ 0.76–0.82 (m, 6H), 1.04–1.35 (m, 24H), 1.54–1.60 (m, 2H), 1.76–1.82 (m, 2H), 3.90–3.98 (m, 5H), 4.11–4.18 (t, $J = 7.4$ Hz, 2H), 7.37–7.40 (m, 1H), 7.51–7.53 (m, 1H), 9.43 (s, 1H). ^{13}C NMR ($CDCl_3$): 13.9, 14.1, 22.3, 22.6, 25.8, 25.9, 29.3, 29.4, 29.51, 29.54, 29.5, 29.6, 29.6, 30.1, 31.0, 31.8, 36.3, 49.9, 67.6, 122.2, 123.9, 137.3. MS (ESI, 20 eV): m/z 167.1 [M–$C_{12}H_{25}OSO_3^-$]$^+$; MS (ESI, 20 eV): m/z 265.0 [$C_{12}H_{25}OSO_3$]$^-$.

ISO 14593-carbon dioxide head space test

To evaluate the biodegradability of the test ILs, the "CO_2 headspace" test (ISO 14593) was applied. This method allows the evaluation of the ultimate aerobic biodegradability of an organic compound in an aqueous medium at a given concentration of microorganisms by analysis of inorganic carbon. The test IL, as the sole source of carbon and energy, was added at a concentration of 40 mg L^{-1} to a mineral salt medium. These solutions were inoculated with activated sludge collected from an activated sludge treatment plant, washed and aerated prior to use and incubated in sealed vessels with a headspace of air. Biodegradation (mineralization to carbon dioxide) was determined by measuring the net increase in the total organic carbon (TOC) levels over time compared with unamended blanks. Sodium *n*-dodecyl sulfate (SDS) was used as a reference substance. The tests ran for 28 days. The extent of biodegradation was expressed as a percentage of the theoretical amount of inorganic carbon (ThIC) based on the amount of test compound.

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