NEW, HALOGEN-FREE IONIC LIQUIDS – SYNTHESIS, PROPERTIES, AND APPLICATIONS

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ABSTRACT

Typical ionic liquids consist of halogen containing anions such as \([\text{AlCl}_4^-]\), \([\text{PF}_6^-]\), \([\text{BF}_4^-]\), \([\text{CF}_3\text{SO}_3^-]\) or \([\text{CF}_3\text{SO}_2\text{N}^+]\). However for many technical applications the presence of halogen atoms in the ionic liquid’s anion may cause serious concerns if the hydrolysis stability of the anion is poor (e.g. for chloroaluminate and hexafluorophosphate systems) or if a thermal treatment of the spent ionic liquid is desired. In both cases additional effort is needed to avoid the liberation of toxic and highly corrosive HF or HCl into the environment. In our contribution, we present synthesis, properties and application of several new alkylsulfate and arylsulfonate ionic liquids. The described systems are characterized by their easy synthesis from technically available raw materials. Some candidates combine low melting points with high hydrolysis stability and acceptable viscosity.

INTRODUCTION

Why Develop Halogen-Free Ionic Liquids?

So far the historical development of ionic liquids has mainly been driven by the combination of different classes of anions with imidazolium, pyridinium, ammonium and phosphonium cations. Chloroaluminate ionic liquids were first described in 1948 by Hurley and Wier at the Rice Institute in Texas as bath solutions for electroplating aluminum (1). Later in the seventies and eighties, these systems were intensively studied by the groups of Osteryoung (2), Wilkes (3), Hussey (4) and Seddon (4b,5).

In 1992, ionic liquid methodology received a substantial boost when Wilkes and Zaworotko described the synthesis of non-chloroaluminate, room temperature liquids, e.g. low melting tetrafluoroborate melts(6). Nowadays, tetrafluoroborate and (the slightly later published) hexafluorophosphate ionic liquids are among the “working horses” in ionic liquid research (7). However, their use in many technical applications is still limited by their relatively high sensitivity vs. hydrolysis. The tendency of anion hydrolysis is of course much less pronounced than for the chloroaluminate melts but still existent. The \([\text{PF}_6^-]\) anion of 1-butyl-3-methylimidazolium ([BMIM]) hexafluorophosphate – for example - has been found in our laboratories to completely hydrolyze after addition of excess water when the sample was kept for 8h at 100°C. HF (toxic and highly corrosive)
and phosphoric acid was formed. Under the same conditions hydrolysis of the tetrafluoroborate ion of [BMIM][BF$_4$] was observed as well, however to a much smaller extend (8). Consequently, the application of tetrafluoroborate and hexafluorophosphate ionic liquids is effectively restricted— at least under a technical scenario - to those applications where water-free conditions can be realized at acceptable costs.

In 1996, Grätzel, Bonhôte and coworkers published synthesis and properties of ionic liquids with anions containing CF$_3$- groups and other fluorinated alkyl groups (9). These do not show the same sensitivity towards hydrolysis than [BF$_4$] and [PF$_6$] containing systems. In fact, heating [BMIM][CF$_3$SO$_2$]$_2$N] with excess of water to 100°C for 24h did not reveal any hint for anion hydrolysis (9).

However, despite the very high stability of these salts against hydrolysis and a number of other very suitable properties (e.g. low viscosity, high thermal stability, easy preparation in halogen-free form due to miscibility-gap with water etc.) the high price of [CF$_3$SO$_2$]$_2$N] and of related anions may be a major problem for their practical application in larger quantities. Moreover, the presence of fluorine in the anion may still be problematic even if hydrolysis is not an issue. Besides the elevated price of the anion (which is also related to the presence of fluorine), the relatively obvious idea to dispose technical amounts of spent ionic liquid by thermal treatment becomes complicated with these ionic liquids. Additional efforts to avoid the liberation of toxic and highly corrosive HF during the combustion of these systems is needed.

A number of halogen-free ionic liquids are already known from the literature. However, none of these systems fulfills the following complex combination of properties that is— according to our experiences - desirable to apply an ionic liquid for potential future bulk applications (heat transfer medium, high performance lubricants, solvent for extraction and extractive distillation). a) melting point or glass point below 40°C; b) thermal stability > 250 °C; c) stability vs. hydrolysis in neutral aqueous solution up to 80°C; d) possible disposal by combustion without formation of highly corrosive gases; e) possible biodegradation of the used anion in ordinary waste water treatment; f) synthesis from cheap, technical available raw materials e.g. alkali salts.

Imidazolium salts with nitrate (6), nitrite (6), sulfate (6), benzensulfonate (10) and phosphonium salts with toluene sulfonate (11) anions are described in the literature but their reported melting points are usually higher then 40 °C. Hydrogensulfate and hydrogenphosphosphate ionic liquids abstract in aqueous solution their protons to form acidic solutions (12). Ionic liquids with methylsulfate and ethylsulfate anions show significant hydrolysis in aqueous solution at 80°C. Hydrogensulfate is formed together with the corresponding alcohol (13).

In this paper we like to give a brief overview of our recent research on new, halogen-free ionic liquids which fulfill the above mentioned technical criteria in a more promising manner. The synthesis and some properties of selected octylsulfate and tosylate ionic liquids will be presented together with preliminary results to use these systems as solvents in the biphasic, Rh-catalyzed hydroformylation of 1-octene.
SYNTHESIS

The principal strategies to synthesize ionic liquids have been published in several review articles (14). In general, the synthesis of an ionic liquid is quite simple organic chemistry while the preparation of an ionic liquid in a certain quality requires some know-how and experience. Since both distillation and crystallization can not be used to purify ionic liquids after their synthesis (due to their non-volatility and low melting points) maximum care has to be taken before and in the ionic liquid synthesis to obtain the desired and reproducible quality.

Moreover, it is well known that impurities in an ionic liquid can have large effects on the physico-chemical properties of the material under investigation (15). For the synthesis of the here described halogen-free ionic liquids we identified the following, potential sources for impurities. a) organic volatiles (e. g. traces of methylimidazol from the synthesis of the chloride salt); b)halide impurities from incomplete metathesis reaction; c) other ionic impurities e. g. resulting from the technical grade raw materials or from some solubility of the used alkali salt in the ionic liquid product; d) water.

In order to obtain reliable data for physico-chemical properties of the here described ionic liquids we took maximum care to either eliminate the impurities completely during synthesis and purification [in case of a)-c)] or to investigate the material with a clearly defined amount of the impurity (in case of water).

Synthesis of Octylsulfate Ionic Liquids

For the synthesis of octylsulfate ionic liquids we started from commercial Na[\(n\text{-C}_8\text{H}_{17}\text{OSO}_3\)] (e. g. 87% purity from Cognis, Düsseldorf/Germany (16), main impurities are inorganic water soluble salts e. g. Na_2SO_4) which is produced in a multi-thousand ton scale as detergent and ingredient for cosmetics. From the technical application of this salt it becomes already quite clear that hydrolysis stability, biological degradation and toxicity of the octylsulfate anion are very well documented.

The anion was combined with the desired cation in a metathesis reaction either from the related chloride salts by precipitation of NaCl (in dry aceton) or by extraction with CH_2Cl_2 from an aqueous solution containing Na[\(n\text{-C}_8\text{H}_{17}\text{OSO}_3\)] and the desired cation (in combination with a highly water soluble anion). The latter method is preferred cause it tolerates water in the sodium salt and allows as well the removal of all ionic impurities originating from the technical quality of the used Na[\(n\text{-C}_8\text{H}_{17}\text{OSO}_3\)]. The synthesis is displayed for a selected example in Scheme 1.

![Scheme 1](image)

**Scheme 1**: Synthesis of octylsulfate ionic liquids.
Toluene sulfonic acid esters are known to be excellent alkylation agents. Some of them are even commercially available. It is therefore quite obvious to synthesize tosylate ionic liquids by direct alkylation of amines or phosphines with the related toluene sulfonic acid ester (Scheme 2). In comparison to ionic liquid synthesis via metathesis, the direct alkylation method avoids the formation of a salt as by-product and reduces drastically the risk of ionic impurities in the final product.

\[
\text{N}^+ \text{Me} + \text{SO}_3\text{Me} \rightarrow \text{[MMIM] [Tosylate]} \quad \text{melting point: 98-101 °C}
\]

\[
\text{N}^+ \text{Bu} + \text{SO}_3\text{Et} \rightarrow \text{[BEIM] [Tosylate]} \quad \text{liquid at RT}
\]

\[
\text{N}^+ \text{Oc} + \text{SO}_3\text{Et} \rightarrow \text{[EOIM] [Tosylate]} \quad \text{melting point: 68-72 °C}
\]

Scheme 2: Selected examples for the synthesis of tosylate ionic liquids by direct alkylation.

**SELECTED PROPERTIES OF ALKYL SULFATE AND ARYL SULFONATE IONIC LIQUIDS**

**Thermal Properties and Viscosity**

Some melting points are already given in Schemes 1 and 2. However, it should be mentioned that some of the described ionic liquids may well be liquid at room temperature even if their melting point is higher than this. For example, \([\text{BMIM}][n\text{-C}_8\text{H}_{17}\text{SO}_3]\) is often obtained as a sub-cooled melt which slowly crystallizes only at temperatures below 5 °C. Another aspect is that only very small amounts of water or other solvents can lower the melting point quite drastically.

Thermal decomposition temperatures of the here described systems is generally high. For example the thermal decomposition temperature of \([\text{BMIM}][n\text{-C}_8\text{H}_{17}\text{OSO}_3]\) was determined by TGA to be 341 °C.

Viscosity is also very dependent on the amount of water and other solvents in the ionic liquid. To produce reliable viscosity date we evacuated every sample at 80°C for 3h at a high vacuum line (10^3 mbar) and we checked the remaining water content by coulometric Karl-Fischer titration using a Metrohm 756 KF Coulometer with a Hydranal® Coulomat AG reagent. In general, we found it very difficult to reduce the water content in large samples to less than 200 ppm. This reflects the highly hygroscopic nature of "dry" octylsulfate and tosylate ionic liquids and gives rise to the question whether anybody would use these systems under absolute dry condition. Therefore, we decided to determine our viscosity data for e. g. \([\text{BMIM}][n\text{-C}_8\text{H}_{17}\text{OSO}_3]\) not in absolute...
“dry” form but with an ionic liquid material of 1000± 100 ppm (0.1±0.01 mass%). The viscosity was determined using a RS 100 viscometer (Haake) and was found to be 874.5 cP at 20°C (as sub-cooled liquid) and 152.3 cP at 50 °C. To compare the viscosity of [BMIM][n-C₈H₁₇OSO₃] to other known solvent systems it may be of interest to note that [BMIM][n-C₈H₁₇OSO₃] reaches at about 45°C the viscosity of [BMIM][PF₆] at room temperature [which is 207 cP according to a paper by Bright et al. (17)] and comes at 100°C close to the room temperature viscosity of ethanediol [16.1 cP according to reference (18)].

Hydrolysis Stability

The lower homologues of alkyl sulfate anions namely methane sulfate and ethane sulfate are known for their sensitivity vs. hydrolysis. In presence of water these anions decompose at elevated temperature to form the corresponding alcohol and hydrgensulfate. Obviously, this process is undesired for most application of the ionic liquid (dramatic change of physico-chemical properties, formation of an acidic proton). For alkylsulfates with longer alkyl groups the sensitivity towards hydrolysis is much lower. Alkylsulfates with 8-18 carbon atoms are used on a multi-million ton scale in detergents, cosmetics and in many other applications where water is omnipresent.

To confirm the expected hydrolysis stability of the new octylsulfate and tosylate ionic liquids we stirred them with the same mass of water at 80°C for several hours and took samples in regular intervals. The pH-values of the aqueous samples were recorded as a probe for the anion’s hydrolysis. While [BMIM] [MeOSO₃] and [EMIM][EtOSO₃] quickly hydrolyze under the conditions of this experiment13 (within the first 30 min), no decrease of pH-value was determined in the case of e.g. [BMIM][n-C₈H₁₇OSO₃] and [BEIM][tosylate] over a period of 8h.

1-Octene Solubility

With regard to an application of the new halogen-free ionic liquids as solvent in the biphasic Rh-catalyzed hydroformylation, we were interested to investigate the solubility of 1-octene in these ionic liquids in more detail (Table 1).

All solvent displayed in Table 1 form biphasic mixtures with 1-octene. While this is a prerequisite for biphasic catalysis, a certain solubility of the substrate in the ionic liquid is required to allow the substrate to reach the catalyst immobilized in the ionic liquid and to realize good reaction rates.

While the solubility of 1-octene in water is too low to allow acceptable hydroformylation rates in a biphasic aqueous reaction system (Table 1, entry i), 1-octene solubility is much higher in the octylsulfate and tosylate ionic liquids. As expected, the solubility of 1-octene in the melt increases markedly with increasing non-polar character of the cation (Table 1, entries a-d). With methyl-tri-n-octylammonium tosylate a single-phase reaction mixture is obtained. A similar cation influence is found for the octylsulfate ionic liquids (Table 1, entries e and f). Remarkably, [BMIM][n-C₈H₁₇OSO₃] shows a much higher 1-octene solubility than the corresponding hexafluorophosphate ionic liquid (comparison of entries f and g).
Table 1: Solubility of 1-octene in different solvents.

| solvent          | solubility 1-octene (mmol/mol) |
|------------------|---------------------------------|
| [MeNEt3] [tosylate]  | 5                               |
| [MeNBu3] [tosylate] | 560                             |
| [MeNPent3] [tosylate] | 1000                           |
| [MeNHex3] [tosylate] | 2319                           |
| [MMIM] [n-C8H17O3S2] | 500                             |
| [BMIM] [n-C8H17O3S2] | 600                             |
| [BMIM] [PF6]2     | 25                              |
| [OMIM] [PF6]2     | 148                             |
| water            | <0.16                           |

1) at 80°C; 2) at 25°C.

Application in Rh-Catalyzed Hydroformylation

Biphasic catalysis is a well-established method for effective catalyst separation and recycling in Rh-catalyzed hydroformylation. This principle has been technically realized in the Ruhrchemie-Rhône-Poulenc-process, where water is used as catalyst phase (19,20,21). Unfortunately, this process is limited to C2-C5-olefins due to the low water solubility of higher olefins. Nevertheless, the hydroformylation of e. g. 1-octene is of technical interest for the synthesis of nonanals.

Already in 1995, Chauvin et al. described the first Rh-catalyzed biphasic hydroformylation using room temperature liquid ionic liquids (22,23). Research efforts in the following years were largely dominated by attempts to improve the immobilization of phosphine ligands in ionic liquids e. g. by using ionic phosphine ligands with cobaltocenium (24), guanidinium (25,26), amidazolium and pyridinium (27) or sulfonate (22) groups.

While all this research was carried out using halogen-containing ionic liquids (mostly hexafluorophosphate ionic liquids), Andersen et al. published in 1998 a paper describing the use of some phosphonium tosylates in the rhodium catalyzed hydroformylation of 1-hexene (11). However, all ionic liquids described in this publications melt at temperatures >70°C which causes serious limitations for a continuous processing of the biphasic reaction.

From all this known work it appeared highly interesting to use our new octylsulfate and tosylate ionic liquids as solvent for the Rh-catalyzed hydroformylation of 1-octene. As catalyst system we used a Rh(CO)2acac precursor in combination with the earlier described (25) phenylguadinium modified triphenylphosphine ligand precursor (Figure 1). Under reaction conditions the anion attached to the phenylguadinium modified triphenylphosphine ligand is readily exchanged by the anion of the ionic liquid.
The results of the hydroformylation experiments are given in Table 2. Surprisingly, we found that the reaction mixture with [BMIM][n-C₈H₁₇OSO₃] does not form a biphasic system any more at high 1-octene conversion. Consequently the reaction mixture becomes monophasic during reaction (Table 2, entry a). Therefore cyclohexane was added as extraction solvent (Table 2, entry b). Under these conditions the biphasic reaction system is maintained even at very high 1-octene conversion and the ionic catalyst solution can be easily separated from the colourless product layer by simple decantation. In contrast, with [BEIM][tosylate] being applied as the solvent, the reaction stays biphasic even at very high 1-octene conversion (Table 2, entry c).

Table 2: Rh-catalyzed hydroformylation of 1-octene in different ionic liquids.

| Ionic liquid | Reaction mode               | TOF (1/h) | n:i-ratio |
|--------------|-----------------------------|-----------|-----------|
| a [BMIM] [n-C₈H₁₇OSO₃] | Monophasic | 892       | 2.86      |
| b [BMIM] [n-C₈H₁₇OSO₃] + cyclohexane | Biphasic | 862       | 2.50      |
| c [BEIM] [tosylate] | Biphasic | 1026      | 2.55      |
| d [BMIM] [PF₆] | Biphasic | 276       | 2.00      |

Conditions: 25-28 bar CO/H₂ (1:1), 100°C, 1 h, 1-octene/Rh = 1000, 5 ml IL, Rh-precursor: Rh(acac)(CO)₂, 2 eq. of ligand precursor 1 as hexafluorophosphate salt.

For all examples displayed in Table 2 the ratio between linear and branched hydroformylation products is between 2 and 3 which is the expected range for triphenylphosphine derived ligands. It is however somewhat unexpected and very interesting, that the activity of the Rh-catalyst is significantly higher with [BMIM][n-C₈H₁₇OSO₃] being the solvent in comparison to commonly used hexafluorophosphate and tetrafluoroborate ionic liquids with the same cation (comparison of examples c and d in Table 2). This may be due to the higher 1-octene solubility in [BMIM][n-C₈H₁₇OSO₃]. Another advantage may arise from the fact that the fluorid anion is known as a poison for the Rh-catalyst and the formation of traces of fluorid during the reaction conditions can not be excluded absolutely if hexafluorophosphate ionic liquids are used.
CONCLUSIONS

Thus our preliminary studies demonstrate that at least some of the new halogen-free ionic liquids are very interesting solvent for the Rh-catalyzed hydroformylation.

Taking into account their much lower cost, their better hydrolysis stability and their wider disposal options in comparison to [BMIM][PF₆] or [BMIM][BF₄], there is no real reason to center future hydroformylation research around hexafluorophosphate and tetrafluoroborate ionic liquids.

For good reasons, ionic liquids are often discussed as ‘green solvents’. Besides their negligible vapor pressure which prevents solvent evaporation into the atmosphere, two additional options are of interest for transition metal catalysis. Firstly, the special solubility characteristics of the ionic reaction medium enables often a biphasic operation mode of the reaction allowing effective separation of the catalyst from the product and catalyst recycling. Secondly, the non-volatile nature of ionic liquids allows a more effective product isolation by distillation.

However, the use of typical ionic liquids consisting of halogen containing anions (such as [AlCl₄]−, [PF₆]−, [BF₄]−, [CF₃SO₃]− or [(CF₃SO₂)₂N]−) restrict in some regard their ‘greenness’. The presence of halogen atoms may cause serious concerns if the anion hydrolyzes under the reaction conditions or if thermal or biological treatment of a spent ionic liquids is desired. In this context, we propose halogen-free octylsulfate and tosylate ionic liquids as promising candidates for many catalytic, biocatalytic and engineering applications. Their technical availability on large scale and their well documented toxicology (at least for the anion part) make these systems especially promising for many of the expected, future industrial application of ionic liquids.

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