ChemComm
www.rsc.org/chemcomm

New, highly acidic ionic liquid systems and their application in the carbonylation of toluene†

Nicole Brausch, Andreas Metlen and Peter Wasserscheid*
Lehrstuhl für Chemische Reaktionstechnik der Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany. E-mail: Wasserscheid@crt.cbi.uni-erlangen.de

Received (in Cambridge, UK) 8th March 2004, Accepted 15th April 2004
First published as an Advance Article on the web 21st May 2004

Based on the surprisingly high solubility of $AlCl_3$ in ionic liquids of type [cation][$(CF_3SO_2)_2N$], a new class of highly acidic, ionic systems has been developed. First tests in toluene carbonylation revealed high potential of these new acidic ionic liquids as catalyst for arene functionaliziation reactions.

In recent years, ionic liquids have attracted much interest as catalysts and alternative solvents for chemical transformations[1]. Chloroaluminate ionic liquids were the first representatives[2] studied in detail and they are still among the best investigated.[3] Since their discovery, these "first generation" ionic liquids have been widely used in the form of their acidic compositions (ratio [cation]Cl/$AlCl_3$ < 1) as catalysts for Friedel–Crafts reactions and similar chemistry.[4] Very recent examples for these on-going and very interesting research activities include *e.g.* Friedel–Crafts addition of arenes to isothiocyanates,[5] oligomerizaton of olefines in ionic liquids[6] or isomerisation reactions of paraffinic feedstocks.[7] As a general conclusion from all acid catalysed reactions with chloroaluminate ionic liquids it can be stated that the aciditiy of the ionic liquid depends on the amount of $AlCl_3$ in the mixed [cation]Cl/$AlCl_3$ system. The higher the amount of $AlCl_3$, the higher is the acidity and hence the catalytic activity of the ionic liquid. However, the amount of $AlCl_3$ in the chloroaluminate system is effectively limited by the liquid range of the ionic liquid to a maximum molar ratio of 2 mol $AlCl_3$ per mol of [cation]Cl.[3]

In the present paper we describe for the first time ionic liquid systems with a considerably higher amount of $AlCl_3$. Our results are based on the surprisingly high solubility of $AlCl_3$ in ionic liquids of the general type [cation][$(CF_3SO_2)_2N$]. This has been found to depend on the structure of the cation and can be in some cases as high as 5 mol $AlCl_3$ per mol of [cation][$(CF_3SO_2)_2N$]! The systems form in a slightly exothermic reaction by simple addition of $AlCl_3$ to a carefully dried bis(trifluoromethanesulfonyl)imide ionic liquid. Even more remarkable, most of these [cation]-[$(CF_3SO_2)_2N$]–$AlCl_3$ mixtures show biphasic behaviour in some specific composition ranges. Typically, a certain (cation dependent) amount of $AlCl_3$ can be homogeneously dissolved in the bis(trifluoromethanesulfonyl)imide ionic liquid up to the lower limit of biphasic regime when a second, colorless and more viscous phase starts to separate. With more added $AlCl_3$ the volume of the lower phase decreases and at the upper limit of the biphasic regime the system starts to become monophasic again. Table 1 shows the lower and upper limits of biphasic behaviour for some examples as well as the maximum solubility of $AlCl_3$ in the system at 80 °C. Fig. 1 displays a photograph of the system [*N*-butyl-4-methylpyridinium][$(CF_3SO_2)_2N$]–$AlCl_3$ = 1 : 2,2 at room temperature.

For the *N*-alkylpyridinium based cations a correlation between the length of the alkyl chain and the lower limit of phase separation can be assumed (see Fig. 1, left). With longer alkyl chains at the nitrogen atom the lower limit of biphasic regime is already reached at significantly lower amounts of $AlCl_3$. Interestingly, all these biphasic systems become monophasic when heated up to 80°C, indicating true thermomorphic behaviour.

To obtain more information about the composition of the two liquid phases, ^1H-, ^{13}C- and ^{19}F-NMR-spectroscopic investigations were carried out for different biphasic compositions of the system [*N*-butyl-4-methylpyridinium][$(CF_3SO_2)_2N$]/$AlCl_3$. The phases were separated after addition of the corresponding amount of $AlCl_3$ to the bis(trifluoromethanesulfonyl)imide ionic liquid and the spectra were recorded in coaxial tubes using d^6-DMSO as external standard. Fig. 2 shows ^{13}C-spectra for the upper and the lower phase of a typical example.

Based on these investigations a first assumption can be made concerning the chemical nature of the two phases. While the upper phase displays the ^{13}C-NMR spectrum expected for the pyridinium cation and the bis(trifluoromethanesulfonyl)imide anion, no cation signals can be found in the lower phase. This indicates that the lower phase is formed by neutral, mixed chloro-[bis(trifluoromethanesulfonyl)imide]-aluminium species. In contrast, the upper phase contains the organic cation and a mixture of chloro-[bis(trifluoromethanesulfonyl)imide]-aluminate ions. This hypothesis could be further confirmed by ion chromatography (IC) and inductive coupling plasma spectroscopy (ICP) analysis.

Table 1 Phase behaviour and maximum $AlCl_3$ solubility for selected [cation][$(CF_3SO_2)_2N$–$AlCl_3$ systems

[Cation]	Lower/upper limit of the biphasic regime[a,b]	Max. $AlCl_3$ solubility[a,c]
1	1.9/2.1	≈ 4.5
2	0.9/2.9	≈ 4.0
3	0.7/2.7	≈ 3.5
4	0.9/2.8	≈ 4.5

[a] Ratio $AlCl_3$/IL (mol/mol). [b] RT. [c] 80 °C, experimental error ± 0.2; **1** = *N*-methylpyridinium; **2** = *N*-hexylpyridinium; **3** = *N,N′*-dimethylimidazolium; **4** = 1-methyl-*N*-pentylimidazolium.

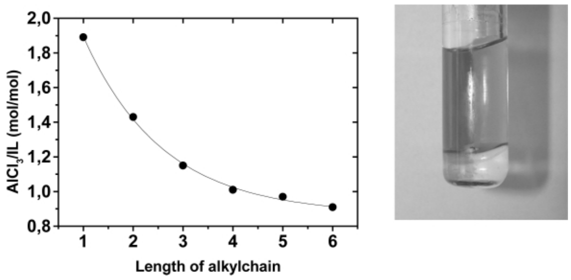


Fig. 1 Left: Correlation between the lower limit of phase separation and the alkyl chain length of alkypyridinium based ionic liquids. Right: Liquid–liquid biphasic system formed in the system [*N*-butyl-4-methylpyridinium][$(CF_3SO_2)_2N$–$AlCl_3$ = 1 : 2.2 at RT.

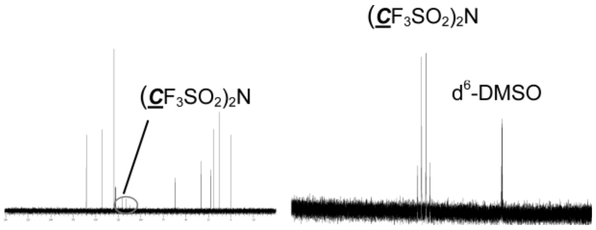


Fig. 2 ^{13}C-spectra of the upper (left) and lower (right) phase from the system [*N*-butyl-4-methylpyridinium][$(CF_3SO_2)_2N$]–$AlCl_3$ = 1 : 2.2

---

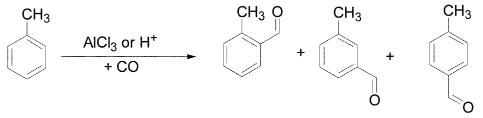
† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b4/b403464c/

DOI: 10.1039/b403464c

To demonstrate the usefulness of our new systems in synthetic applications we decided to study the carbonylation of toluene as a test reaction (see Scheme 1). The reaction is known to require highly acidic catalysts systems to obtain any conversion at all. The carbonylation of toluene has been previously studied by Knifton[8] and Saleh[9] using classical imidazolium and pyridinium chloroaluminate ionic liquids. Our catalytic results are displayed in Table 2. In this context, it is important to note that all mixtures [cation][$(CF_3SO_2)_2N$]–$AlCl_3$ in our catalytic experiments were homogeneous, monophasic systems under the conditions of the experiment. However, the catalytic transformation was carried out as a biphasic reaction due to the limited solubility of toluene in the acidic ionic liquid. The product isolation was carried out by a hydrolysis step followed by extraction with cyclohexane to guarantee proper product analysis.

The results show a clear dependency from the ionic liquid's cation with a maximum yield in tolualdehyde for the ethyl substituted pyridinium cation. This is attributed to solubility effects, taking into account that the reaction requires both sufficient solubility for toluene and CO in the catalyst layer.

Most interestingly we could demonstrate that the [cation]-[$(CF_3SO_2)_2N$] can be isolated and recycled after the hydrolysis of the reaction mixture due to the hydrolytical stability and the hydrophobicity of the bis(trifluoromethanesulfonyl)imide anion. The recovered [cation][$(CF_3SO_2)_2N$ could be reloaded with $AlCl_3$ and reused in the catalysis without loss in activity or selectivity. We are convinced that the easy recycling of the quite expensive cation component is an important advantage in comparison to the well-known chloroaluminates (where an aqueous waste containing the organic cation is obtained in the hydrolysis step).



Scheme 1 Carbonylation of toluene

Table 2 Carbonylation of toluene using ionic liquid/$AlCl_3$ systems[a]

Ionic liquid (IL)	$AlCl_3$/IL (mol/mol)	Yield tolualdehyde[b]	% Sel.[c]
[**1**][$(CF_3SO_2)_2N$]	2.5	21.67	85.8
[**2**][$(CF_3SO_2)_2N$]	2.5	12.85	84.8
[**5**][$(CF_3SO_2)_2N$]	2.5	29.51	85.9
[**6**][Cl][d]	1.0	7.5	88,0

[a] *Conditions: T* = 80 °C, *p*(CO) = 70 bar, 2 h, $AlCl_3$ to toluene 1 : 1 (50 mmol). [b] Isolated yield %. [c] Selectivity to *para*-tolualdehyde in all tolualdehydes; **1** = *N*-methylpyridinium; **2** = *N*-hexylpyridinium; **5** = *N*-ethylpyridinium [d] Comparison with[8] **6** = *N*-butylpyridinium; conditions: *T* 100 °C, *p*(CO) 204 atm, 4 h, [**6**]/[$AlCl_4$] to toluene 1 : 1.

In conclusion we have reported for the first time new highly-acidic ionic liquid systems based on [cation][$(CF_3SO_2)_2N$]–$AlCl_3$ mixtures. These systems show interesting cation and temperature dependent phase behaviour as well as surprisingly high solubilities for $AlCl_3$. For the carbonylation of toluene we could demonstrate their potential as highly acidic, liquid catalysts.

Finally, we assume that the usefulness of the systems described here might be not restricted to classical synthetic applications. The high $AlCl_3$ solubility combined with the known wide electrochemical window of the bis(trifluoromethanesulfonyl)imide ionic liquids[10] may open up other interesting applications such as *e.g.* for Al electroplating. Furthermore, preliminary studies suggest that the observed solubility of $AlCl_3$ in ionic liquids of the type [cation] bis(trifluoromethanesulfonyl)imide may be not a unique feature of this specific Lewis acid. For example $SbCl_3$, $SbCl_5$ and $GaCl_3$ also show high solubility in [*N*-butyl-4-methylpyridinium] [$(CF_3SO_2)_2N$].

BMBF (N.B.) and Novartis Foundation (A.M.) are gratefully acknowledged for financial support for this project.

Notes and references

1 Comprehensive information about this field can be found in many recent reviews: T. Welton, *Chem. Rev.*, 1999, **99**, 2071; P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772; H. Olivier-Bourbigou and L. Magna, *J. Mol. Catal. A: Chem.*, 2002, **182/3**, 419; P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, 2003; S. A. Rorsyth, J. M. Pringle and D. R. MacFarlane, *Aust. J. Chem.*, 2004, **57**, 113.
2 F. H. Hurley and T. P. Wier, *J. Elektrochem. Soc.*, 1951, **98**, 207.
3 A. A. Fannin, D. A. Floreani, L. A. King, J. S Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes and J. L. Williams, *J. Phys. Chem.*, 1984, **88**, 2614.
4 M. Earle in P. Wasserscheid and T. Welton (Eds.), *Ionic Liquids in Synthesis*, Wiley-VCH: Weinheim, 2003.
5 P. U. Naik, S. J. Nara, J. R. Harjani and M. M. Salunkhe, *Can. J. Chem.*, 2003, **81**, 1057.
6 O. Stenzel, R. Brull, U. M. Wahner, R. D. Sanderson and H. G. Raubenheimer, *J. Mol. Catal. A: Chem.*, 2003, **192**, 217.
7 K. Herbst, J. Houzvicka, B. J. Tofte and J. Zavilla, US 2003181780.
8 J. F. Knifton, US 4554383, (Texaco Inc. White Plains. N. Y.), [*Chem. Abstr*. 1985, 104, 129634].
9 R. Saleh, WO 2000015594, (Exxon Chemicals Inc.); [*Chem. Abstr*. 2000, 132, 222341].
10 P. Bonhote, A. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Armand and M. Graetzel, *Inorg. Chem.*, 1996, **35**, 1168.