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Synthesis and characterization of ionic liquids based upon 1-butyl-2,3-dimethylimidazolium chloride/$ZnCl_2$

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Trialkylimidazolium chlorozincate molten salts resulting from the combination of zinc chloride and 1-butyl-2,3-dimethylimidazolium chloride, [BMMI][Cl], have been prepared with a mole percent of $ZnCl_2$, R ($R = n_{ZnCl_2}/n_{ZnCl_2} + n_{[BMMI][Cl]}$) equal to 0, 0.1, 0.25, 0.33, 0.5, 0.66, 0.75. Their analyses by DSC, ^{13}C, ^{1}H and ^{35}Cl solid state and solution NMR, and mass spectrometry (ESI, MS/MS) are consistent with the presence of [BMMI][Cl] and [BMMI][$ZnCl_3$] for $R < 0.5$; pure [BMMI][$ZnCl_3$] for $R = 0.5$, and [BMMI][$ZnCl_3$] with [BMMI][Zn_3Cl_7] for $R > 0.5$. Infrared spectra realized in the presence of pyridine show that the Lewis acidity of $ZnCl_2$–[BMMI][Cl] increases with R. High temperature (110 °C) ^{13}C and ^{35}Cl NMR experiments on neat [BMMI][$ZnCl_3$] ($R = 0.5$) evidenced that its structure varies with time from [BMMI][$ZnCl_3$] to [BMMI···Cl···$ZnCl_2$].

Introduction

Application of ionic liquids in biphasic catalysis has blossomed within the last decade and has been driven by the need for environmentally friendly solvents. Comprehensive information about the latest developments may be found in recent reviews.[1–7] Most importantly, it is possible to tune the physical and chemical properties of ionic liquids by varying the nature of the cations and the anions.[7] In particular, depending on the coordinative properties of the anion or/and activity of the cation, ionic liquids can be considered as both the solvent and co-catalyst or as the catalyst itself. Indeed, the development of acidic ionic liquids, derived from metal halides, as replacements for traditional acids has received significant attention.[7–13] Currently, two types of ionic liquids are largely developed: those based on chlorometallate anions and those based on non-metal-containing anions, such as BF_4^- and $(CF_3SO_2)_2N^-$.[8] This paper is focused on the former, which are reviewed below, in order to demonstrate that most of the metal chlorides, even with a low acidity, can form, with any organic halide, a salt with a low melting point. We also emphasize the fact that few of them can afford polynuclear anions.

The *n*-butylpyridinium salts with $AlCl_3$ were described as the first room temperature molten salt.[14] Similar results were obtained with *n*-alkylimidazolium salts as cations.[15] Chloroaluminate anions have been widely characterized, by NMR spectroscopy (^{27}Al, ^{31}P and ^{1}H),[9,11,16,17] Raman scattering,[18] and by other techniques such as UV and IR spectroscopies and electrochemical methods.[19,20] Depending on the relative proportion of $AlCl_3$, several equilibria were evidenced, however, only two anions are coexisting. Above 3 equiv. $AlCl_3$ is in excess and could be sublimed:

$$Cl^- + AlCl_3 \leftrightarrow AlCl_4^-$$
$$AlCl_4^- + AlCl_3 \leftrightarrow Al_2Cl_7^-$$
$$Al_2Cl_7^- + AlCl_3 \leftrightarrow Al_3Cl_{10}^-$$

The acidity of these ionic liquids refers to the acidity of an anionotropic solvent system, in which a base is a substance that liberates Cl^- while an acid consumes it.[16] The polynuclear anions, such as $Al_2Cl_7^-$, are acidic because they contain an excess of $AlCl_3$, which can be neutralized with nonmetal chlorides such as KCl:

$$Al_2Cl_7^- + M^+Cl^- \rightarrow 2AlCl_4^- + M^+$$

The water sensitivity of chloroaluminate led to use numerous other anhydrous metal salts. However, few gave materials that were liquid below 100 °C.[21]

Only in the case of $FeCl_3$, $ZnCl_2$ and $SnCl_2$ was the formation of polynuclear anions reported. With $FeCl_3$, Raman scattering indicated the presence of $FeCl_4^-$, then the formation of $Fe_2Cl_7^-$ when $FeCl_3$ is in excess. With $FeCl_2$ the only observed iron-containing species was $FeCl_4^{2-}$. In the mixed melts containing both $FeCl_3$ and $FeCl_2$, only the mononuclear anions $FeCl_4^-$ and $FeCl_4^{2-}$ were formed.[22–23] With $SnCl_2$ and $ZnCl_2$, for a ratio of 2 : 1 relative to the cation, $SnCl_3^-$ and $Sn_2Cl_5^-$ and $ZnCl_3^-$, $Zn_2Cl_5^-$, $Zn_3Cl_7^-$, respectively, were identified by negative FAB mass spectra.[21,24,25] In contrast, CuCl, $InCl_3$, $AuCl_3$ and $TeCl_4$ with imidazolium chloride

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formed only monometal chloride anions, $CuCl_2^-$, $AuCl_4^-$, $TeCl_6^{2-}$ and $InCl_4^{-1}$.[26,27]

The preparation of ionic liquids using zinc chloride with pyridinium,[28] quaternary ammonium salt,[21,24,29] and imidazolium salts has been reported.[30–33] These ionic liquids, less water sensitive than the chloroaluminate analogues, were used for zinc and zinc alloy deposition,[34] in a Friedel–Craft reaction,[35] regiospecific synthesis of Fisher indole,[36] and for various catalytic reactions.[37–41] Generally, ionic liquids containing zinc chloride as the anion improved the catalytic results. This can be explained at least in part by the fact that the zinc chloride anion is a co-catalyst. For example, the best conversion and selectivity in the isomerization of 2-methyl-3-butenenitrile into 3-pentenenitrile,[40,41] were obtained with 1-butyl-2,3,-dimethyimidazolium [BMMI] as the counter-cation and chlorozincate as the anion.[42] However, structural properties and the presence of a Lewis acidic centre in ionic liquids using zinc chloride has not yet been clearly established.[43]

In this paper we report the synthesis of molten salts resulting from the combination of zinc chloride and 1-butyl-2,3-dimethylimidazolium chloride, [BMMI][Cl], and their characterization by DSC, ^{13}C, ^{1}H and ^{35}Cl solid state and solution NMR, at variable temperature, and mass spectrometry (ESI, MS/MS).

Experimental

Materials and methods

All operations were performed in the strict absence of oxygen and water under a purified argon atmosphere using glove box (Jacomex or M Braun) or vacuum line techniques. Under argon, solvents were distilled using the appropriate drying agents: pyridine from CaH_2 and acetonitrile-d_3 (99% deuterium) from P_2O_5 and stored over molecular sieves. $ZnCl_2$ (99.999%, H_2O < 100 ppm) was obtained from Aldrich and dehydrated with trimethylchlorosilane before use.[44] 1-Chlorobutane and 1,2-dimethyimidazole, obtained from Aldrich, were freshly distilled before use. 1-Butyl-2,3-dimethylimidazolium chloride [BMMI][Cl] was synthesized as described in the literature.[45]

DSC procedures. The differential scanning calorimetry (DSC) experiments used a Mettler DSC 12 apparatus. DSC traces were typically scanned from 10 or 25 °C to 300 °C at a speed of 10 °C min^{-1}. Each sample was allowed to equilibrate for several minutes at 10 or 25 °C before the scan was initiated. All scans were done using increasing temperature only and were highly reproducible. Each peak of in the DSC traces indicates a transition temperature of the $ZnCl_2$–[BMMI][Cl] mixture of a given compositions. In the glove box, samples of up to 40 mg were sealed in aluminum crucibles. For ionic liquids showing transition phase peaks, a second identical ramping of the temperature after cooling was performed.

^{1}H,^{13}C, ^{35}Cl liquid NMR. Solution NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer for ^{1}H and ^{13}C and a DRX 500 MHz instrument for ^{35}Cl. Chemical shifts were measured relative to $SiMe_4$ as internal standard for ^{1}H and ^{13}C and relative to external HCl (0.1 M in H_2O) for ^{35}Cl. The sample for ^{35}Cl NMR was prepared as follows: [BMMI][Cl] or [BMMI][$ZnCl_3$] ($R = 0.5$) was introduced in a NMR tube (5 mm) in the glove box. Then, the NMR tube was put inside a Schlenk tube, which was heated, under argon, until the compounds were liquefied and then put under vacuum for 1 h. A capillary of DMSO-d_6 was introduced under argon into the molten solid.

^{1}H and ^{13}C solid state NMR. Solid state NMR spectra were recorded on a Bruker DSX-300 spectrometer equipped with a standard 4 mm double-bearing probe head and operating at 75.47 and 300.18 MHz for ^{13}C and ^{1}H, respectively. ^{13}C NMR spectra were recorded as follows: 30° pulse on ^{13}C nuclei and acquisition under a 80 KHz decoupling field on protons, with 1 s recycle delay and 5 KHz spinning speed unless otherwise specified.

Mass spectrometry. Mass spectra were acquired on a ThermoFinnigan LCQ Advantage ion trap instrument, detecting positive and negative ions in the electrospray ionization (ESI) mode. Samples (1 to 10 μg ml^{-1} in acetonitrile) were infused directly into the source (5 μl min^{-1}) using a syringe pump. The following source parameters were applied: spray voltage 3.0–3.5 kV, nitrogen sheath gas flow 5–20 arbitrary units. The heated capillary was held at 200 °C. MS spectra were obtained by applying a relative collision energy of 25–40% of the instrumental maximum.

Infrared spectroscopy. Infrared spectra were recorded on a Nicolet 550 FT spectrometer by using a liquid infrared cell equipped with KBr windows. Typically, 16 scans were accumulated for each spectrum. Pyridine (4 μl) was added to 0.1 M of ionic liquids in CD_3CN, in order to obtain a molar ratio of pyridine to ionic liquid equal to 1.

Preparation of ionic liquids

The ionic liquids over the whole range of compositions, that is with a $ZnCl_2$ mole fraction in the mixture $R = n_{ZnCl_2}/(n_{ZnCl_2} + n_{[BMMI][Cl]}) = 0.10$, 0.25, 0.33, 0.50, 0.66 and 0.75, were prepared by addition, at 105 °C, of $ZnCl_2$ into molten [BMMI][Cl] under a dry argon atmosphere. As an example, for the synthesis of [BMMI][$ZnCl_3$] with $R = 0.5$, anhydrous zinc dichloride (2.73 g, 0.02 mol) was slowly added under argon into melted 1-butyl-2,3-dimethylimidazolium chloride (3.8 g, 0.02 mol) and the mixture was stirred at 105 °C for 12 h.

***R* = 0.5.** ^{13}C NMR (CD_3CN, δ): 145.40 (s, C_2), 123.43 and 121.95 (d, $C_{4,5}$), 48.99 (s, C_8), 35.83 (s, C_6), 32.39 (s, C_9), 20.16 (s, C_{10}), 13.83 (s, C_7), 10.25 (s, C_{11}). ^{13}C Solid-state NMR (δ): 146.66 (C_2), 123.24 and 122.23 ($C_{4,5}$), 49.59 (C_8), 34.59 (C_6), 32.07 (C_9), 21.92 (C_{10}), 15.06 (C_7), 12.34 (C_{11}). MS (*m*/*z* for the major peak with ^{35}Cl) ESI^+: 153.1 $[BMMI]^+$ (100%), 340.8 $[(BMMI)_2Cl]^+$ (56.9%). ESI^-: 410.9 $[(BMMI)_2Cl_3]^-$ (100%), 600.8 $[(BMMI)_3Cl_4]^-$ (65.0%), 788.8 $[(BMMI)_4Cl_5]^-$ (25.0%), 976.9 $[(BMMI)_5Cl_6]^-$ (10.0%).

***R* = 0.1.** [BMMI][Cl] (5 g, 26.5 mmol); $ZnCl_2$ (0.402 g, 2.95 mmol). ^{13}C NMR (CD_3CN, δ): 145.42 (s, C_2), 123.45 and 121.95 (d, $C_{4,5}$), 49.00 (s, C_8), 35.87 (s, C_6), 32.39 (s, C_9), 20.16 (s, C_{10}), 13.84 (s, C_7), 10.30 (s, C_{11}). ^{13}C Solid-state NMR (δ): 146.66 (C_2), 123.24 and 122.23 ($C_{4,5}$), 48.08 (C_8), 37.8 (C_6), 32.07 (C_9), 21.92 (C_{10}), 15.06 (C_7), 12.34 (C_{11}). MS (*m*/*z* for the major peak with ^{35}Cl) ESI^+: 153.1 $[BMMI]^+$ (100%), 340.8 $[(BMMI)_2Cl]^+$ (11.2%). ESI^-: 171.0 $[Zn^{35}Cl_3]^-$ (15.3%), 410.9 $[(BMMI)_2Cl_3]^-$ (50.7%), 600.8 $[(BMMI)_3Cl_4]^-$ (95.9%), 788.8 $[(BMMI)_4Cl_5]^-$ (87.7%), 976.9 $[(BMMI)_5Cl_6]^-$ (100%).

***R* = 0.25.** [BMMI][Cl] (4.073 g, 21.61 mmol); $ZnCl_2$ (0.9815 g, 7.2 mmol). ^{13}C NMR (CD_3CN, δ): 145.42 (s, C_2), 123.46 and 121.94 (d, $C_{4,5}$), 49.03 (s, C_8), 35.94 (s, C_6), 32.38 (s, C_9), 20.17 (s, C_{10}), 13.85 (s, C_7), 10.34 (s, C_{11}). ^{13}C Solid-state NMR (δ): 146.66 (C_2), 123.24 and 122.23 ($C_{4,5}$), 49.59 and 48.08 (C_8), 37.8 and 34.59 (C_6), 32.07 and 31.22 (C_9), 21.92 and 19.07 (C_{10}), 15.06 and 14.68 (C_7), 12.34 and 11.32 (C_{11}). MS (*m*/*z* for the major peak with ^{35}Cl) ESI^+: 153.1 $[BMMI]^+$ (100%), 340.8

$[(BMMI_2Cl]^+$ (5.3%). ESI$^-$: 171.0 $[ZnCl_3]^-$ (41.5%), 410.9 $[(BMMI)_2Cl_3]^-$ (67.1%), 600.8 $[(BMMI)_3Cl_4]^-$ (100.0%), 788.8 $[(BMMI)_4Cl_5]^-$ (94.1%), 976.9 $[(BMMI)_5Cl_6]^-$ (80%).

***R* = 0.33.** [BMMI][Cl] (4.07 g, 22 mmol); $ZnCl_2$ (1.47 g, 11 mmol). ^{13}C NMR (CD_3CN, δ): 145.41 (s, C_2), 123.47 and 121.94 (d, $C_{4,5}$), 49.07 (s, C_8), 36.00 (s, C_6), 32.37 (s, C_9), 20.18 (s, C_{10}), 13.85 (s, C_7), 10.38 (s, C_{11}). ^{13}C Solid-state NMR (δ): 146.66 and 145.79 (C_2), 123.24 and 122.23 ($C_{4,5}$), 49.59 and 48.08 (C_8), 37.8 and 34.59 (C_6), 32.07 and 31.22 (C_9), 21.92 and 19.07 (C_{10}), 15.06 and 14.68 (C_7), 12.34 and 11.32 (C_{11}). MS (m/z for the major peak with ^{35}Cl) ESI$^+$: 153.1 $[BMMI]^+$ (100%), 340.8 $[(BMMI)_2Cl]^+$ (2.9%). ESI$^-$: 171.0 $[ZnCl_3]^-$ (100%), 410.9 $[(BMMI)_2Cl_3]^-$ (57.1%), 600.8 $[(BMMI)_3Cl_4]^-$ (74.3%), 788.8 $[(BMMI)_4Cl_5]^-$ (75.7%), 976.9 $[(BMMI)_5Cl_6]^-$ (35.7%).

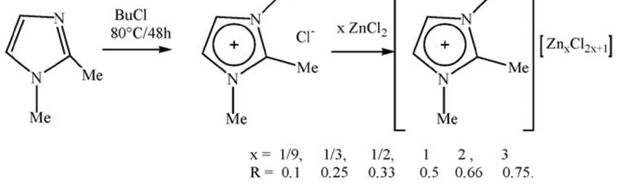
***R* = 0.5.** [BMMI][Cl] (3.8 g, 20 mmol); $ZnCl_2$ (2.73 g, 20 mmol). ^{13}C NMR (CD_3CN, δ): 145.41 (s, C_2), 123.35 and 121.87 (d, $C_{4,5}$), 49.06 (s, C_8), 35.94 (s, C_6), 32.34 (s, C_9), 20.17 (s, C_{10}), 13.81 (s, C_7), 10.30 (s, C_{11}). ^{13}C Solid-state NMR (δ): 145.79 (C_2), 124.05 and 121.47 ($C_{4,5}$), 48.08 (C_8), 37.8 (C_6), 31.22 (C_9), 19.07 (C_{10}), 14.68 (C_7), 11.32 (C_{11}). MS (m/z for the major peak with ^{35}Cl) ESI$^+$: 153.1 $[BMMI]^+$ (100%), 340.8 $[(BMMI)_2Cl]^+$ (4.7%). ESI$^-$: 171.0 $[ZnCl_3]^-$ (100%).

***R* = 0.66.** [BMMI][Cl] (2.54 g, 13.5 mmol); $ZnCl_2$ (3.71 g, 27 mmol). ^{13}C NMR (CD_3CN, δ): 145.42 (s, C_2), 123.31 and 121.85 (d, $C_{4,5}$), 49.05 (s, C_8), 35.90 (s, C_6), 32.32 (s, C_9), 20.15 (s, C_{10}), 13.82 (s, C_7), 10.29 (s, C_{11}). ^{13}C Solid-state NMR (δ): 144.81 (C_2), 122.88 and 119.01 ($C_{4,5}$), 49.28 and 48.08 (C_8), 35.49 (C_6), 31.22 (C_9), 20.30 (C_{10}), 14.68 (C_7), 11.32 (C_{11}). MS (m/z for the major peak with ^{35}Cl) ESI$^+$: 153.1 $[BMMI]^+$ (100%), 340.8 $[(BMMI)_2Cl]^+$ (6.5%). ESI$^-$: 171.0 $[ZnCl_3]^-$ (100%), 306.6 $[Zn_2Cl_5]^-$ (44.1%), 442.4 $[Zn_3Cl_7]^-$ (85.3%).

***R* = 0.75.** [BMMI][Cl] (1.64 g, 8.68 mmol); $ZnCl_2$ (3.55 g, 26.05 mmol). ^{13}C NMR (CD_3CN, δ): 145.39 (s, C_2), 123.30 and 121.84 (d, $C_{4,5}$), 49.05 (s, C_8), 35.91 (s, C_6), 32.31 (s, C_9), 20.19 (s, C_{10}), 13.83 (s, C_7), 10.29 (s, C_{11}). ^{13}C Solid-state NMR (δ): between 146.62 and 144.25 (m, C_2), between 126.00 and 118.13 (m, $C_{4,5}$), between 48.48 and 48.14 (C_8), 34.57 (C_6), 31.22 (C_9), 20.02 (C_{10}), 14.68 (C_7), 11.32 (C_{11}). MS (m/z for the major peak with ^{35}Cl) ESI$^+$: 153.1 $[BMMI]^+$ (100%), 340.8 $[(BMMI)_2Cl]^+$ (8.2%). ESI$^-$: 171.0 $[ZnCl_3]^-$ (61.2%), 306.6 $[Zn_2Cl_5]^-$ (42.9%), 442.4 $[Zn_3Cl_7]^-$ (100%).

Results

The ionic liquids have been synthesized by the slow addition of solid anhydrous $ZnCl_2$ into melted [BMMI][Cl], eqn. (1), x was the number of equivalents of $ZnCl_2$ *versus* [BMMI][Cl], and R, the mole ratio of $ZnCl_2$.



(1)

DSC (differential scanning calorimetry)

Table 1 shows the DSC transition temperatures (to the nearest degree), thermal decomposition temperatures and liquidus ranges of the $ZnCl_2$–[BMMI][Cl] mixtures. According to Table 1, for each ionic liquid, the melting point is lower than 100 °C, the thermal decomposition is above 210 °C and the liquidus range between 125 °C and 210 °C. Both the decomposition temperature and liquidus range roughly increase with R. For all liquids except $R = 0$ and 0.5, cooling from the liquid state caused glass formation. For $R = 0.5$, an initial transition temperature was observed at 58.7 °C. This transition is not reversible, but was reproducible for independently prepared samples. Similar observations have already been reported with 1-alkyl-3-methylimidazolium tetrachloropalladate(II) salts.[46]

Table 1 Transition temperatures, thermal decomposition temperatures and liquidus ranges from DSC thermograms of the $ZnCl_2$–[BMMI][Cl] mixtures for various mole ratios R

	Transition temperature/°C						
R	Peak 1	Peak 2	Peak 3	Peak 4	M.p./°C[a]	θ_{decomp}/°C	Liquidus range[b]/°C
0	104.6	—	—	—	104.6	230	125.4
0.1	64	97.5	—	—	97.5	240	142.8
0.25	68.2	—	—	—	68.2	240	171.8
0.33	56.4	69.5	85.8	98.1	69.5	210	140.5
0.5	58.7	90.8	—	—	90.8	>300	209.2
0.66	—	—	—	—	78.0[c]	>300	222.0
0.75	88.4	—	—	—	88.4	280	191.6

[a] The melting point corresponds to the most intense peak in the DSC trace. [b] Corresponds to the temperature range between melting and decomposition. [c] For R = 0.66, m.p. was measured on a digital electrothermal melting point apparatus.

^1H, ^{13}C solution NMR

The cation $BMMI^+$ can be a probe to study the nature of the ionic liquid. For this purpose, solutions of the different ionic liquids in the same solvent (CD_3CN) and at the same concentration and temperature (0.1 mol l^{-1}, 25 °C), were analysed by ^1H, ^{13}C NMR.

In ^{13}C NMR, the evolution of the chemical shift of carbons C_2, C_7, C_8, C_9, C_{10} and C_{11} is not significant ($\Delta\delta < 0.1$). However, the chemical shifts of the ethylenic carbons C_4 and C_5 move towards higher field as R increases and they can be roughly classified into three series, one for $R < 0.5$, one for

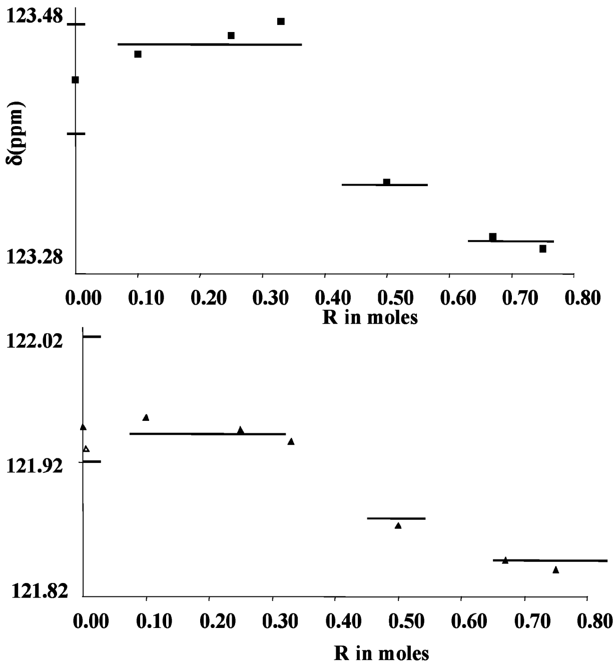


Fig. 1 Variation of the ^{13}C NMR chemical shifts of C_4 (top) and C_5 (bottom) as a function of R (CD_3CN, 0.1 mol).

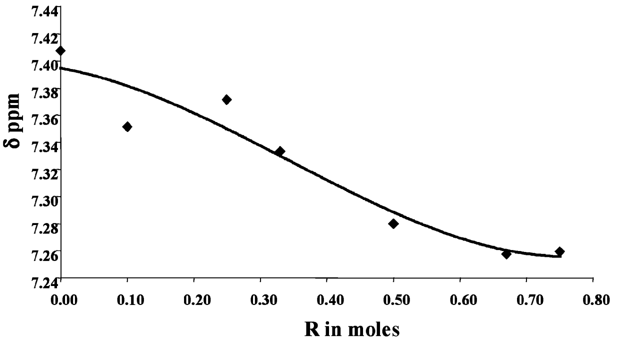


Fig. 2 Variation of the ^1H NMR chemical shifts of H_4 and H_5 as a function of *R* (CD_3CN, 0.1 mol).

$R = 0.5$ and one for $R > 0.5$ (Fig. 1), indicating that there are at least three different chemical environments for the imidazolium cation.

In ^1H NMR spectra, the chemical shifts of the ethylenic hydrogens H_4 and H_5 exhibit a monotonous decrease as *R* increases (Fig. 2). In 1-butyl-3-methylimidazolium chlorozincate [BMI][Zn_xCl_{2x+1}], the chemical shift of C_2–H shows a variation due to a possible hydrogen bond between the anion and the hydrogen atom on C_2 of the imidazolium ring.[33] Similarly, in the case of [BMMI][Zn_xCl_{2x+1}], the hydrogen bond could occur between the anion and the hydrogen atoms H_4 and H_5.

^{13}C solid state NMR at 25 °C

The evolution of chemical shifts in ^{13}C solid state NMR, as a function of *R*, of the cation $BMMI^+$ is given in Fig. 3. The most significant variations of chemical shifts were observed in the interval 0–70 ppm.

The solid state ^{13}C NMR spectrum of [BMMI][Cl] is depicted in Fig. 3, spectrum a, in which the characteristic peaks are labelled by "o". In the region 0–70 ppm, a set of six peaks corresponds to the resonance of carbon C_{6-11} (δC_6 34.6, , δC_7 15.1,, δC_8 49.6, δC_9 32.1,, δC_{10} 21.9, δC_{11} 12.3) of the imidazolium. The peaks between 100 and 150 ppm are attributed to C_2 (146.6 ppm), C_4 (123.2 ppm) and C_5 (122.2 ppm).

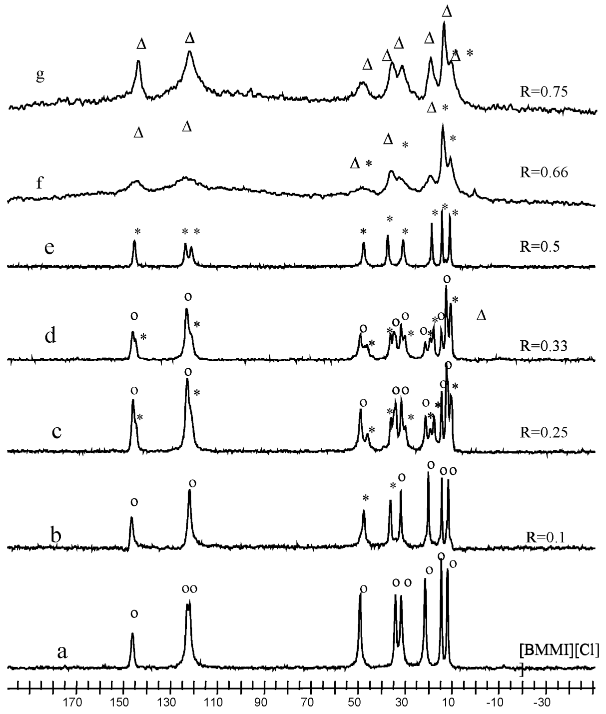
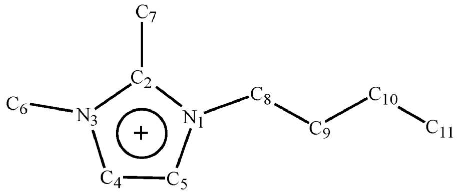


Fig. 3 ^{13}C solid state NMR spectra of [BMMI][Zn_xCl_{2x+1}] as a function of *R* at 25 °C.



For the values of $R = 0.1$, 0.25 and 0.33 (Fig. 3, spectra b–d), besides the resonances of [BMMI][Cl] (o), another set of six peaks (labelled *) appeared. These intensity of these peaks increases with *R* and for $R = 0.5$ only these resonances are present (Fig. 3, spectrum e). Then, for $R = 0.66$ and $R = 0.75$, even if the peaks were broad, the presence of a new set of six peaks (labelled Δ) could be noticed (Fig. 3, spectra f and g). Therefore, a comparison of the spectra in Fig. 3 clearly evidences three sets of six peaks (o, * and Δ) but only two sets are present at any given value of *R*. These ^{13}C solid state NMR spectra suggest that, at 25 °C for $R = 0$ and $R = 0.5$, there is a single product, [BMMI][Cl] and [BMMI][Zn_xCl_y], respectively. In contrast, for $R < 0.5$, the obtained ionic liquids are a mixture of these two products, the ratio of [BMMI][Zn_xCl_y] : [BMMI][Cl] increasing with *R*. For ionic liquids with $R > 0.5$, there is no longer any [BMMI][Cl].

ESI mass spectrometry

Electrospray ionization mass spectroscopy (ESI/MS) is a very useful tool for the analysis of ionic liquids[47a] and to determine the nature of catalytic species present in it.[47b] Positive and negative ESI mass spectra of the [BMMI][Cl]–$ZnCl_2$ ionic liquids with various compositions were recorded in order to determine the nature of these ionic liquids.[8]

In positive mode (ESI^+), for all ionic liquids the most intense peak occurs at *m*/*z* 153.1, corresponding to the $[BMMI]^+$ ion. The peak of the ion $[(BMMI)_2Cl]^+$ at $m/z = 340.8$, which decreases in intensity as *R* increases is absent for $R \geq 0.5$. The clusters $[(BMMI)_nCl_{n-1}]^+$ are observed only for $R = 0$ and 0.1.

In negative mode (ESI^-) the negative clusters due to the presence of Cl^- and $Zn_xCl_y^-$ anions are observed. No peaks corresponding to oxohalogenated species such as $ZnOCl^-$ (*m*/*z* 117), $Zn_2OCl_3^-$ (*m*/*z* 252), and $Zn_3OCl_5^-$ (*m*/*z* 388) are apparent.[20]

For ionic liquids with $R < 0.5$, the chloride ions being in excess, it was expected that Zn(II) would be present mainly as $ZnCl_4^{2-}$. However, the isotopic pattern corresponding to $ZnCl_4^{2-}$ ($m/z = 104$) is not observed. In contrast, the isotopic pattern corresponding to $ZnCl_3^-$ ($m/z = 171$) is always present, even for $R = 0.1$. Furthermore, the cluster anions $[(BMMI)_xCl_{x+1}]^-$ observed in ESI^- mass spectra of pure [BMMI][Cl] are present in the spectrum of ionic liquids with $R < 0.5$ and disappear totally for $R = 0.5$. The intensity of the isotopic pattern due to $ZnCl_3^-$ increases monotonously with *R* to reach 100% for $R = 0.33$, 0.5 and 0.66, and then sharply decreases to 60% for $R = 0.75$, which reveals that $ZnCl_3^-$ is still the main Zn(II) species. For $R = 0.66$, the peaks corresponding to the anions $Zn_2Cl_5^-$ ($m/z = 306.6$) and $Zn_3Cl_7^-$ ($m/z = 442.4$) simultaneously appear. The intensity of the peak corresponding to $Zn_3Cl_7^-$ varies from 85% to 100% for $R = 0.6$ and 0.75, respectively; in contrast, the intensity of the peak corresponding to $Zn_2Cl_5^-$ stays constant (≈44%) for $R = 0.6$ and 0.75.

A MS/MS experiment on the peak at $m/z = 414$ of the isotopic pattern corresponding to $Zn_3Cl_7^-$ gave the isotopic pattern corresponding to $Zn_2Cl_5^-$. This result supports the fact that $Zn_2Cl_5^-$ could be formed during the fragmentation of $Zn_3Cl_7^-$, which is coherent with the simultaneous appearance of the two anions when $R > 0.5$. While $Zn_3Cl_7^-$ is present in the media, the formation of $Zn_2Cl_5^-$ is not proven by this

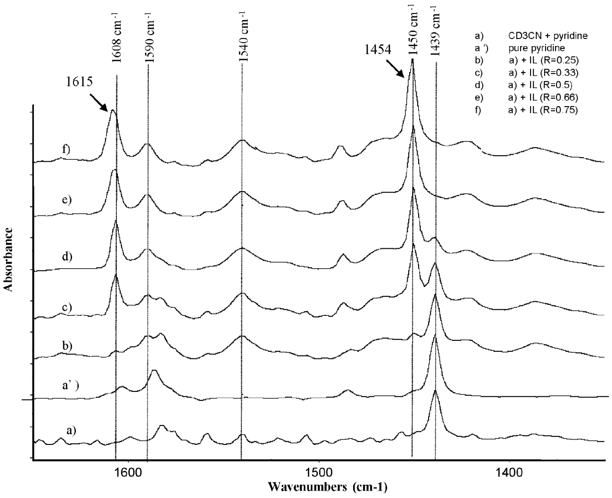


Fig. 4 IR spectra [4 μL of pyridine were added to 0.1 M ionic liquids (IL) in CD_3CN, in order to obtain molar ratios of pyridine *vs* ionic liquid equal to 1] of a) CD_3CN + pyridine, a′) subtraction of CD_3CN bands; of solution of [BMMI][Cl]–ZnCl2 + pyridine in CD_3CN b) R = 0.25, c) R = 0.33, d) R = 0.5, e) R = 0.66, f) R= 0.75.

analysis. However, the ESI^- results indicate that for $R < 0.5$ only the anions Cl^-, $ZnCl_3^-$ are present, for $R = 0.5$ there is a single anion $ZnCl_3^-$, and for $R > 0.5$ there is no Cl^-, but a mixture of chlorozincates $ZnCl_3^-$, $Zn_3Cl_7^-$ and perhaps $Zn_2Cl_5^-$.

Determination of Lewis acidity

Pyridine has been used as a probe molecule for the determination of the Lewis acidity of the synthesized chlorozincate ionic liquids by monitoring, in the infrared spectra, the bands in the 1400–1700 cm^{-1} region arising from its ring vibrational modes.[48,49] Fig. 4 depicts the infrared spectra obtained from a solution of [BMMI][Cl]–$ZnCl_2$ and pyridine (molar ratio 1 : 1) in CD_3CN for different values of R. In the infrared spectra, CD_3CN shows overlapping of bands in the 2400–2200 cm^{-1} region [ν(CN) and ν(CD)] while in the 1650–1400 cm^{-1} region there are no parasite bands (see spectrum a in Fig. 4). However, firstly there is coordination of CD_3CN on the Lewis acidic centre as reported in the literature,[43] then due to the large excess of pyridine (ratio pyridine : ionic liquid = 1) a partial ligand exchange occurs between acetonitrile and pyridine, which allows the Lewis acidic character of these ionic liquids to be determined from the evolution of the band at 1439 cm^{-1}. When R increases, the band at 1439 cm^{-1} decreases and finally disappears completely for R = 0.66 (spectra b–e in Fig. 4). Simultaneously, for R = 0.25 two bands at 1446 and 1608 cm^{-1}, spectrum b in Fig. 4, appear and shift to 1454 and 1615 cm^{-1}, respectively, for R = 0.75 (Fig. 4, spectrum f). These bands are characteristic of pyridine coordinated to Lewis acid sites. This acidity increases with R. These results are in accordance with the literature.[43] A band near 1540 cm^{-1} is also present and is an indication of the formation of pyridinium ion resulting from the presence of Brønsted acidic sites, probably due to residual protons.

Evolution of the structure of [BMMI][$ZnCl_3$] with temperature

The ^{13}C solid state NMR spectra of neat [BMMI][Cl] and neat [BMMI][$ZnCl_3$] were obtained at 25 and 100 °C (Fig. 5). At 25 °C (Fig. 5, top) the spectra of the two ionic liquids are different in pattern and chemical shifts, while they become identical at 100 °C (Fig. 5, bottom).

The ^{35}Cl liquid NMR spectra of neat [BMMI][Cl] and [BMMI][$ZnCl_3$] were obtained at 110 °C. The $\delta^{35}{}_{Cl}$ chemical shifts of [BMMI][Cl] and [BMMI][$ZnCl_3$] are 84 and 800 ppm, respectively. However, the very broad peak due to the chlorine resonance of [BMMI][$ZnCl_3$] at 800 ppm at t = 0 shift to 400 ppm in 20 min, then moves more slowly to 250 pm after 60 min, then stays unchanged (Fig. 6).

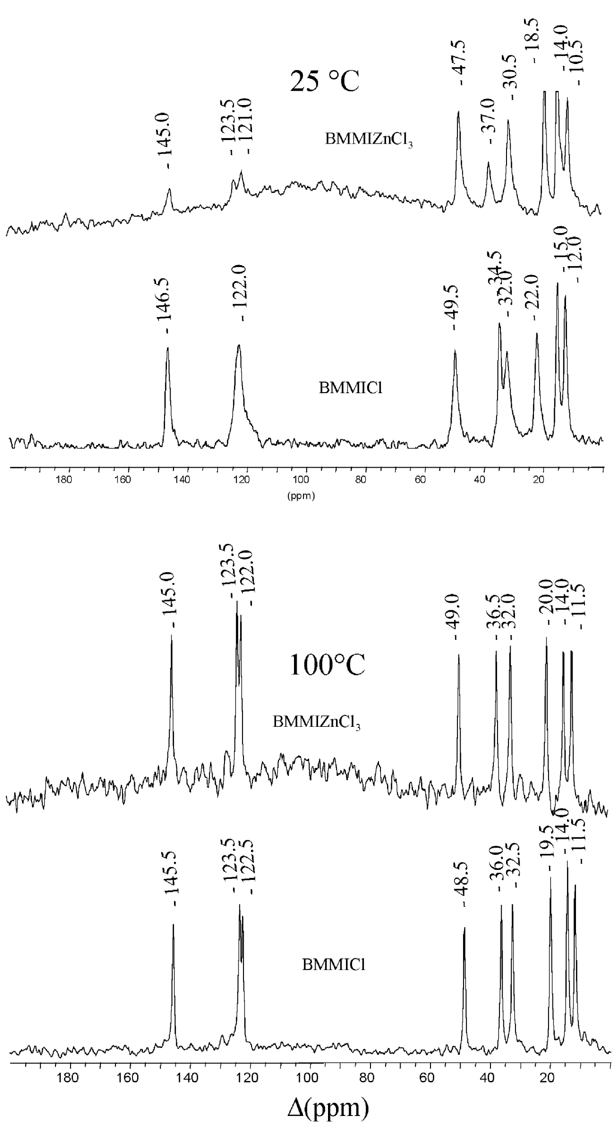


Fig. 5 ^{13}C NMR spectra of [BMMI][Cl] and [BMMI][$ZnCl_3$] at 25 °C (top) and 100 °C (bottom).

These observations were reversible and reproducible for independently prepared samples. These results from ^{35}Cl NMR corroborate those of the ^{13}C NMR. There is an evolution of the structure of the ionic liquid [BMMI][$ZnCl_3$] at 100–110 °C towards a dissociated structure such as [BMMI···Cl···$ZnCl_2$].

Discussion

The mass spectrometry results indicate that, for $0 \leq R \leq 0.5$, only the anions Cl^- and $ZnCl_3^-$ are present. Yet, for these value of R the ^{13}C solid state NMR spectra show that the ionic liquids with $R = 0$ and $R = 0.5$ correspond to a single product, [BMMI][Cl] and [BMMI][Zn_xCl_y], respectively, and that those with $0 < R < 0.5$ are a mixture of these two products, the ratio [BMMI][Zn_xCl_y] : [BMMI][Cl] varying with R. It can be deduced from these two analyses that only the species [BMMI][Cl] and [BMMI][$ZnCl_3$] are present when $0 \leq R \leq 0.5$. With these ionic liquids having $R \leq 0.5$, in the presence of pyridine the wavenumber of the band corresponding to coordination at the Lewis acid sites was 1450 cm^{-1}, indicating a Lewis acid character of these ionic liquids.

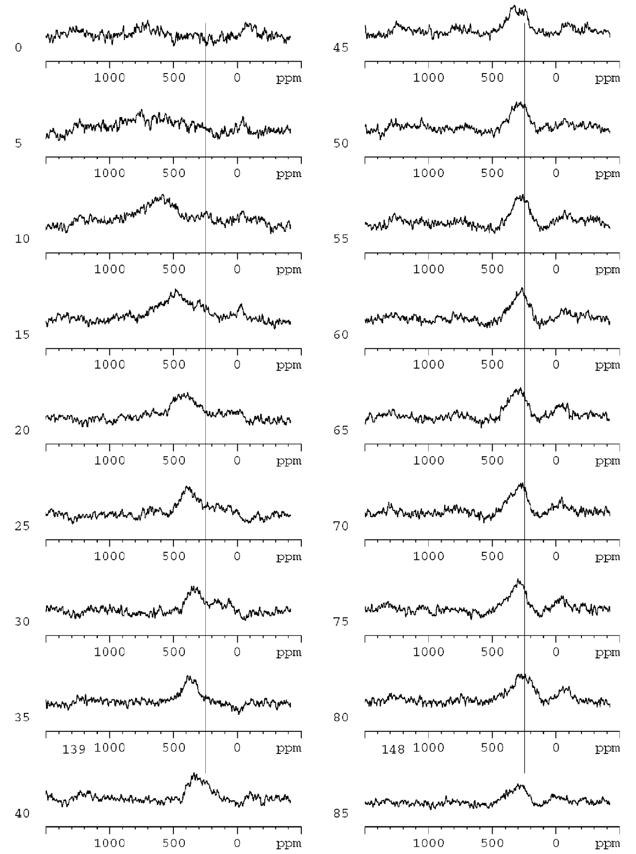


Fig. 6 ^{35}Cl NMR spectra of [BMMI][$ZnCl_3$] at 110 °C as a function of time (min).

For the ionic liquids with $R > 0.5$ the anions $ZnCl_3^-$ and $Zn_3Cl_7^-$ were unambiguously identified. However, the presence of $Zn_2Cl_5^-$ cannot be totally excluded in spite of the MS/MS experiment results. For these values of R, due the broadness of the peak in the ^{13}C solid state NMR spectra (spectrum f in Fig. 3), it is only possible to conclude that there is no [BMMI][Cl] while [BMMI][$ZnCl_3$] is still present for $R = 0.66$. However, for $R = 0.75$ the DSC results show a sharp melting point (88.4 °C), the resonance due to [BMMI][$ZnCl_3$] in the ^{13}C solid state NMR spectra (spectrum g in Fig. 3) is minor, and in the presence of pyridine the wavenumber of the bands corresponding to coordination at Lewis acid sites are clearly different at 1454 and 1618 cm^{-1}, which allows us to propose at this point that the $Zn_3Cl_7^-$ anion becomes predominant. Therefore, when $R > 0.5$, two species are mainly present: [BMMI][$ZnCl_3$] and [BMMI][Zn_3Cl_7]. Note that the pyridine molecular probe can differentiate between $ZnCl_3^-$ and $Zn_3Cl_7^-$ by coordination at the different acidic sites.

The results of ^{35}Cl and of ^{13}C NMR indicate an evolution of the structure of the ionic liquid [BMMI][$ZnCl_3$] at 100–110 °C towards a dissociated structure such as [$BMMI\cdots Cl\cdots ZnCl_2$]. These results clearly establish that this reaction is reversible as a function of temperature and consequently that Cl^- anions and free $ZnCl_2$ are present in the media. This is fundamental information because we have recently demonstrated that there is an exchange reaction between the cations of the ligand and of the ionic liquids when Cl^- anion is present in the solution, leading to an evolution of the nature of the coordination sphere of the catalyst.[50] Stated otherwise, the organization of ions in ionic liquids has an influence on their interaction with the unsaturated substrate and consequently on their reactivity. These results could be very useful for the understanding of some catalytic results and underlines the importance of polynuclear anions that sequester free Cl^- anions.

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