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Bromozincate ionic liquids in the Knoevenagel condensation reaction

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ABSTRACT

Ionic liquids (ILs) have been widely promoted as functional replacements of volatile organic solvents; however restricting their use to conventional solvents constrains their potential. One means of enhancing their utility is through the development of dual purpose ILs, capable of acting as both solvent and catalyst. A series of bromozincate ILs was synthesised, and the Lewis acidities probed spectroscopically. Furthermore, the crystal and molecular structure of $[C_2Py]_2[ZnBr_4]$ was determined through single-crystal X-ray diffraction. The ILs were then used in a model reaction, aimed at probing effects of both IL Lewis acidity and structural organisation on the reaction outcome.

1. Introduction

Currently, most non-aqueous solvents used in industrial applications are major contributors to industrial waste and pose detrimental effects to both human health and the environment. Ionic liquids (ILs) have received widespread attention as an environmentally benign alternative to organic solvents in a variety of reaction systems, due to their recyclability, low vapour pressure and low flammability resulting in a reduction in hazards associated with solvent use. Moreover, the large number of potential anion and cation combinations allows for an extensive variety in tailorable functionalities [1–5].

In addition to directly influencing the solvation environment, ILs have been shown to exhibit distinctive internal structural features, such as the formation of heterogeneous structures, i.e. with the segregation of polar and non-polar domains [6,7]. This domain segregation, referred to as nano-segregation is one of the features that distinguishes ILs from the homogeneous environment of organic solvents, and offers an approach to control the characteristics of a reaction (rate, selectivity etc.) through IL modification. As demonstrated by both simulation [8,9] and experiment [10], polar solutes will preferentially solvate in the polar domain and non-polar solutes in the non-polar domains of ILs, permitting the encapsulation or partitioning of solutes in specific domains. This phenomenon has been shown to significantly affect chemical reactivity [10], it is frequently overlooked.

An extension of the use of ILs as solvents, is the development of dual purpose ILs, such that a single IL may act as both catalyst and solvent [11]. Several Lewis acidic ILs have been used previously as dual purpose solvents and catalysts, the most common the chloroaluminate anion [12,13]. However issues with handling and synthesis limit the practical use of this class of material. The work reported here outlines the use of bromozincate ILs [14] which overcome handling barriers and offers an affordable and more environmentally benign alternative to more corrosive and reactive materials. We also report the influence of Lewis acidity and internal organization of these ILs on a model reaction. The cations used and the corresponding abbreviations employed throughout this work are depicted in Fig. 1.

2. Experimental

2.1. Chemical reagents

The following reagents were used as received: benzaldehyde, pyridine (both Ajax), anhydrous zinc bromide, 1-bromobutane, 1-bromohexane, 1-bromodecane, 1,2-dimethylimidazole, 1-methylimidazole (Aldrich), malononitrile (Alfa), *p*-isopropyltoluene (> 99%; Fluka), 1-bromoethane, 1-bromooctane (both Merck). Diethyl ether, hexane and dichloromethane (DCM) were deoxygenated and dried over activated alumina, using an apparatus modified from that described in the literature [15].

2.2. Ionic liquid synthesis

Bromide containing ILs were synthesised using standard literature methods [16]. The syntheses of bromozincate containing ILs were based on a synthetic approach from Abbott et al. [17]. The desired bromide salt (8.9 mmol) was mixed with anhydrous zinc bromide ($ZnBr_2$, 8.9 mmol), and heated to 60 °C under nitrogen. The resulting compound was then cooled and washed with diethyl ether (2 × 10 mL),

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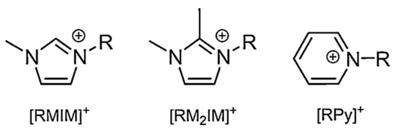

Fig. 1. Schematic illustrations and nomenclature of cations used in this work, where R = $(CH_2)_{n\text{-}1}CH_3$, n = *2, 4, 6, 8, 10.*

and hexane (10 mL) and dried under vacuum, yielding the desired bromozincate IL. A list of ILs prepared in this work and their full physical characterisation data including ^{1}H NMR, ^{13}C NMR, DSC, TGA and ± ESI/MS are available in the ESI. Water content of the ILs was determined using a Karl Fischer coulombic titrator (Mettler Toledo) and was found to be ≤10 ppm.

2.3. Ionic liquid characterisation

2.3.1. X-ray crystallography

Colourless blade-like crystals of [C_2Py]Br/$ZnBr_2$ were grown on standing the IL in methanol for 24 h. The crystal structure was solved in the monoclinic space group $C_{2/c}$ by direct methods with SHELXT [18] and extended and refined with SHELXL-2014/7 [19], with the formula resolved to be $[C_2Py]_2[ZnBr_4]$. Refer to ESI for further details.

2.3.2. Computational predictions through density functional theory

Density functional theory (DFT) quantum chemical calculations were performed with Gaussian 09 [20]. Geometries and energy densities were obtained at the M05-2X/6-31G(d) level, combined with the SMD continuum solvation model [21,22]. Acetonitrile solvation parameters were used in the SMD model. Vibration frequencies of stationary points corresponded to the minima on the potential energy surface. Incorporated into the total energies are zero-point vibrational energies and thermal corrections for enthalpy and entropy derived from scaled M05-2X-D3/6- 31G(d) frequencies [23]. All free energies (kJ mol^{-1}) are reported as solvation-corrected at 298 K, and charges on zinc were calculated using natural bond orbital (NBO) analysis.

2.3.3. Raman spectroscopy

Raman spectra were recorded on a Renishaw Raman Reflex inVia spectrometer fitted with a Leica DMLM microscope. A 514 nm laser was used over the range: 100–2000 cm^{-1}, with a resolution of 4 cm^{-1}. Absorption maximum values were obtained by direct peak picking from raw spectra.

2.3.4. Lewis acidity determination of bromozincate ILs

The Lewis acidity of the ILs was spectroscopically probed with pyridine in a similar method to that previously reported by Yang et al. [24]. Samples were prepared with a mass ratio of pyridine to IL (1:3). FT-IR spectra were obtained using a thin film method with sodium chloride cells on a Bruker Vertex 80V FTIR Spectrometer over the range 1600 and 1400 cm^{-1} at room temperature, with a resolution of 0.2 cm^{-1}. Three repeat scans were performed and the spectra averaged.

2.4. Knoevenagel condensation reactions

2.4.1. Synthesis of 2-benzylidenemalononitrile

For calibration 2-benzylidenemalononitrile was synthesised as follows: Benzaldehyde (2 g, 19 mmol) was mixed with malononitrile (1.25 g, 19 mmol) and heated at 80 °C for 4 h. The yellow crystals formed were washed with water, and recrystallized from methanol, to yield fine white crystals of 2-benzylidenemalononitrile (2.23 g, 24 mmol, 65%, m.p. 82–85 °C). ^{1}H NMR ($CDCl_3$, ppm) δ 7.90 (m, 2H), 7.61 (m, 1H), 7.78 (s, 1H), 7.54 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): δ 163.1, 129.1, 127.0, 126.2, 111.7, 82.5.

2.4.2. Knoevenagel catalysis condensation reactions

All ILs were dried *in vacuo* at 60 °C for 4 h prior to use. ILs (2.0 mL,φ_{IL} = 0.99) were heated in a Schlenk flask to 95 °C (internal temperature) prior to the addition of benzaldehyde (1.5×10^{-4} mol, 15 μL) and malononitrile (1.5×10^{-4} mol, 8 μL), with an internal standard of *p*-cymene (5 μL). All sample volumes were maintained at a total volume of 2.028 mL. The sample was then extracted with methanol (5 mL) and passed through a silica column before analysis on a Shimadzu GC-2010 Plus, fitted with a Restek Rtx-5MS column (30 mm × 0.25 mm, I.D.; 0.25 μm thickness) and a Shimadzu AOC-20i auto injector, a split ratio of 10 was used, with a 2.0 mL min^{-1} flow rate. Analysis was performed on Real Time analysis software. The conversions of substrate were determined by comparisons with a calibration curve established with 2-benzylidenemalononitrile (synthesis outlined in Section 2.4.1.).

3. Results and discussion

3.1. Structural characterization of bromozincate ILs

Single crystal X-ray diffraction analysis of the while solid precipitate of [C_2Py]Br/$ZnBr_2$ revealed an asymmetric unit cell composed of a tetrabromozincate dianion and two ethylpyridinium cations, of formula $[C_2Py]_2[ZnBr_4]$ (Fig. 2 (a), refer to ESI for crystallographic details).

Bromozincate anions of types $[ZnBr_4]^{2-}$ [25,26], $[Zn_2Br_6]^{2-}$ [14,27,28], and $[Zn_2Br_7]^{3-}$ [14] have been structurally characterised. However the structural characterisation of $[C_2Py]_2[ZnBr_4]$ is yet to be reported. Similar to previous characterisations, the dianion was shown to have a central zinc atom in a tetrahedral environment, with an average Br–Zn–Br angle of 109.4°, and average Zn—Br bond length of 2.417(3) Å. Each anion is surrounded by 8 cations, through the formation of 14 Br···H bonds. The average Br···H contact distance is 3.02(1) Å, less than the sum of the van der Waals radius (3.05 Å), indicating close interactions between the anion and cation. The Br···H interactions are not uniformly distributed for each bromide atom with the number of contacts varying between 2 and 5 contact points, indicating that several anion–cation interactions are stabilizing the structure.

An extended crystal structure viewed along the *b* axis, is shown in Fig. 2(b). The 3D network appears to be composed of two separate cation environments. One cation environment is composed of sheets orientated parallel to the *ab* plane, and are stabilized by close intermolecular quadrupole interactions between neighbouring pyridinium rings, with an average contact distance of 3.603(2) Å. The other cation environment forms planar sheets orientated parallel to the *ac* plane, and is stabilized by anion interactions, with no cation–cation interactions being present.

3.1.1. Lewis acidity of bromozincate ionic liquids

Lewis acidities of the ILs were studied to establish the relationship between activity and acidity. Using pyridine as a spectroscopic probe, the determination of Lewis acidity was achieved through examination of variations in the frequencies of the ring vibration absorptions [24]. Although this is technique does not measure the lewis acidity of the bulk IL, it can be used as a means determine relative Lewis acidities of the ILs used in this work.

As shown in Fig. 3, neat pyridine shows a resolved single absorption at 1437 cm^{-1}, resulting from the in-plane vibration of symmetry class B_1 [29]. With the addition of a Lewis acid shifts in absorption maxima are observed, due to the coordination of Lewis acidic sites with pyridine. Greater shifts in absorption maxima correspond to stronger Lewis acids.

As some ILs are solid at room temperature only a selected range of ILs were analysed for Lewis acidity. Consequently, a representative sample set, including [C_6MIM]Br/$ZnBr_2$, [C_6M_2IM]Br/$ZnBr_2$ and [C_6Py]Br/$ZnBr_2$ was used (Fig. 3). Fig. 3 (c), shows that a pyridine