Novel imidazolinium ionic liquids and organic salts

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ABSTRACT

The preparation and physical properties of a novel family of ionic liquids and organic salts based on the imidazolinium cation are described, and compared with their imidazolium analogues in some cases. Ionic liquids were obtained with the triflate, formate and salicylate anions, while > 100 °C melting points were observed with acetate and several other benzoate derivatives. The triflate salt was less ion-conductive than the corresponding imidazolium salt, but less so than expected on the basis of its viscosity, suggesting a contribution from proton conductivity. The electrochemical window of the imidazolinium was slightly extended in the reductive direction, due to the lower proton activity produced by the cation in this case. Imidazolinium salts are also known to exhibit anti-corrosion properties and hence a preliminary study of this property is also reported; 2-methylimidazolinium 4-hydroxycinnamate was found to show strong anodic corrosion inhibition on mild steel.

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1. Introduction

As a class of materials, ionic liquids (ILs) are generally classified as salts with melting points below 100 °C [1]. Due to the vast number of cations and anions that can be combined to form ILs, they can have greatly varying properties and, as such, ionic liquid research spans a broad range of fields. This includes, but is not limited to, investigation of their use in electrochemical devices [2] and as "green" solvents [3].

Recently this has begun to include development of ILs for use in corrosion protection of metals. Corrosion is an insidious problem that annually causes trillions of dollars' worth of damage worldwide [4]. While a variety of corrosion inhibitors exist, many, such as the extremely effective chromates, are highly toxic [5]. Ionic liquids are being sought that could provide "greener" alternatives for use on a range of metals. One approach is to use ionic liquid pre-treatments to form passivating films on the metal surface. This is particularly useful for protection of reactive metals such as magnesium and aluminium [6]. To date this work has focused predominantly on phosphonium based ILs [7,8].

A number of publications have also investigated the use of ionic liquids as additive chemical inhibitors, with a particular focus towards protecting steel in acidic environments, a common industrial condition. A range of imidazolium cations have been

tested, including traditional alkyl methylimidazoliums [9,10] and novel substituted cations [11,12], as well as other cations such as pyridinium [12] and pyridazinium [13].

Most of these examples rely on the use of conventional ILs, despite one of the greatest strengths of the IL platform being the ability in principle to design a compound or a formulation for a given application. In recent years, there has been a shift in the focus of this tuneability. Initial investigations into ILs looked to alter physical properties such as viscosity and thermal stability. Eventually this evolved to tailoring not only the physical properties, but the chemical properties as well, to develop ILs that were chiral [14,15] or strong coordinating solvents [16]. The 'third generation" of ILs, as proposed by Rogers and coworkers [17] introduced the idea of manipulating their biological properties. This concept does not, however, have to be limited to pursuing pharmaceutical compounds, but rather can be seen as a shift in the way component ions are chosen. Instead of trying to fit traditional ILs to a given application, one can take an "active" compound and redesign it as an IL with enhanced functionality for a range of applications where bio-activity, or biocompatibility is important. In some of our previous work [18,19] we have shown how ionic liquids and salts developed this way can tackle the insidious problem of microbially induced corrosion, by combining known antibacterial agent ions with corrosion inhibiting counter ions.

From our continued investigation of such compounds we present here a novel family of task-oriented organic salts and ionic liquids featuring the 2-methylimidazolinium [2-MeHImn]+ cation. We describe a range of salts of this cation, some in particular

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targeted towards use as corrosion inhibitors. Imidazolines and their salts, some of which are liquids, are known and used in a number of industries, notably as corrosion inhibitors, particularly in oil pipelines [20,21]. The compounds often feature lengthy fatty-acid functional groups and in those cases can be classified as cationic surfactants [20–22]. As can be seen in Fig. 1, imidazolinium cations are closely related to the more broadly recognised imidazolium cations, with the only difference to the core ring being the saturation of the C4-C5 double bond. Despite this similarity, the imidazolinium cation has not been widely explored in the IL context (for any application) and thus it appears to offer a promising avenue for new IL chemistry. Thus we present here a number of novel ionic liquids and organic salts based on this cation and investigate their properties including an initial investigation of their corrosion inhibition activity.

2. Experimental

2.1. Materials

All chemicals were purchased from Sigma and were >98% pure. They were used without further purification. Methanol was distilled from sodium metal and stored over 4 Å molecular sieves, acetonitrile and dichloromethane were dried over 4 Å molecular sieves.

2.2. Synthetic Methods

2.2.1. Synthesis of 2-methylimidazolinium acetate

Triethylorthoacetate (10.5 mL, 53 mmol) and acetic acid (3.1 mL, 53 mmol) were added to a flask of acetonitrile. Ethylenediamine (3.4 mL, 50 mmol) was added slowly via a dropping funnel, resulting in formation of a white precipitate. The mixture was heated to reflux and stirred under N_2 for 2 h, causing dissolution of the precipitate. The solvent was removed by rotary evaporation, with further drying under high vacuum to give a pale yellow solid (6.50 g, 90%). ^{1}H NMR (400 M Hz, DMSO-$d6$) δ (ppm): 1.67 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 3.73 (unresolved d, 4H, 2x CH_2). ^{13}C NMR (400 M Hz, DMSO-$d6$) δ (ppm): 12.75 (CH_3), 25.13 (CH_3), 45.17 (2x CH_2), 169.01 (N−C=N), 177.90 (C=O). Mass spectrum: ES$^+$ m/z 85.0 [2-MeHImn]$^+$; ES$^-$ m/z 58.9 [Ac]$^-$.

2.2.2. Synthesis of 2-methylimidazolium triflate

2-methylimidazole (1.6 g, 20 mmol) was dissolved in acetonitrile. Triflic acid (3.3 g, 22 mmol, diluted in acetonitrile) was added slowly and the mixture stirred at room temperature under nitrogen for 3 h. The solvent was removed via rotary evaporation and the product dried under high vacuum at 60 °C to yield a pale pink solid (4.6 g, 98%). ^{1}H NMR (400 MHz, DMSO-$d6$) δ (ppm): 2.07 (s, 3H, CH_3), 3.73 (unresolved d, 4H, 2x CH_2). ^{13}C NMR (400 MHz, DMSO-$d6$) δ (ppm): 11.16 (CH_3), 118.70 (2x CH), 144.29 (N−C=N). ^{19}F NMR (400 MHz, DMSO-$d6$) δ (ppm): 77.77. Mass spectrum: ES$^+$ m/z 83.1 [2-MeHIm]$^+$, 315.1 2[2-HMeHIm]$^+$[Tf]$^-$; ES$^-$ m/z 148.9 [Tf]$^-$, 380.9 [2-MeHIm]$^+$2[Tf]$^-$.

Synthesis of further compounds contained in the supplementary information.

2.3. Analysis

The purity of the samples was determined using NMR and mass spectrometry. NMR spectra were recorded in DMSO-$d6$ (Merck) using a Bruker Avance 400 (9.4 T magnet) operating at 400 MHz. Low resolution ESI mass spectra were recorded on a Micromass Platform II QMS with a cone voltage of 35 V, using methanol as the mobile phase.

The ILs were dried thoroughly under high vacuum prior to physical property measurements and the presence of water was not detected during characterisation of these samples (ie. TGA). Karl Fischer titration was found to be an inaccurate means of testing the water content of the samples as the ILs reacted in the titration vessel.

Differential scanning calorimetry was carried out using a Perkin Elmer DSC 8000 with liquid nitrogen cryo cooler. Scans were run at a heating/cooling rate of 10 °C/min over a temperature range of −80 to 250 °C. Transition temperatures were reported using the peak maximum of the thermal transition.

Thermogravimetric analysis was undertaken on a Mettler Toledo TGA/DSC 1 STARe System. Samples were heated at 10 °C/min over a temperature range of 25 to 450 °C.

Density measurements were performed using an Anton Paar DMA 5000 Density Meter. This meter uses the 'oscillating U-tube principle' to determine density. Viscosity measurements were undertaken using an Anton Paar Lovis 2000 M microviscometer. This instrument uses the falling ball technique. Measurements were taken from 90 °C until the materials solidified. The conductivity was evaluated using AC impedance spectroscopy over a range of 20 Hz to 1 MHz. Measurements were carried out using a Hewlett Packard 4284 LCR meter. Resistance values for conductivity calculations were taken to be the data point closest to the x-axis on the impendance plot.

Cyclic voltammetry was carried out using a multi-channel potentiostat (VMP2, Princeton Applied Research). Samples were dissolved in acetonitrile and used as the electrolyte in a three-electrode system with platinum working and counter electrodes and a non-aqueous Ag/Ag$^+$ reference. Measurements were carried out at a scan rate 20 mV s^{-1}.

For the potentiodynamic polarisation experiments AS1020 steel electrodes (composition: 0.26% C, 0.45% Mn, 0.14% Cr, 0.19% Si, 0.18% Al, 0.35% other, and balance Fe) with a 1.0 cm diameter (0.78 cm^2) set in epoxy resin were used. They were abraded with silicon carbide paper to P4000 grit from P320 grit. The electrodes were washed with distilled water, dried and stored in a desiccator under vacuum. Potentiodynamic polarisation experiments were carried out half an hour after electrode preparation.

The test solutions were prepared by dissolving the appropriate masses of each compound in 1 L of 0.01 M sodium chloride solution (made with milliQ water) to make concentrations of 4 mM. The pH of these solutions ranged from 5.9–7.0.

All polarisation experiments were carried out in an open-to-air, standard three-electrode system consisting of a saturated calomel reference electrode (SCE), a titanium mesh counter electrode, and the working electrode with 150 mL of test solution as the electrolyte. The cell assembly was located in a Faraday cage to prevent electrical interference.

After immersion the open circuit potential (OCP) was monitored for 30 minutes, and then the potentiodynamic polarisation experiment was carried out at a scanning rate of 0.167 mV s^{-1}. The scans started at 100 mV more negative than E$_{corr}$ and continued through E$_{corr}$ for a range of 400 mV in the positive direction. Measurements were carried out in triplicate. All electrochemical
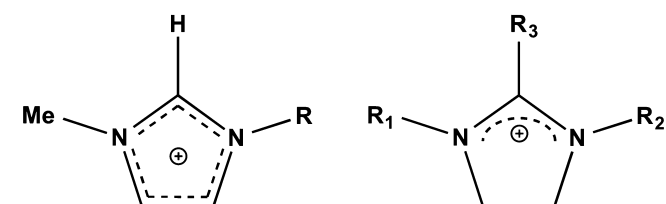

Fig. 1. A comparison of the common ionic liquid cation methylimidazolium and the general structure of the imidazolinium cation.