



Ionic liquid binary mixtures: Promising reaction media for carbohydrate conversion into 5-hydroxymethylfurfural

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ABSTRACT

The conversion of carbohydrates into 5-hydroxymethylfurfural (5-HMF) has been studied in binary mixtures of ionic liquids (ILs), using strongly acidic resin Amberlyst 15 as the catalyst. In particular, both mono- and disaccharides, such as fructose, glucose and sucrose have been investigated. Considering the favorable effect exerted by chloride-based ionic liquids in the dissolution of carbohydrates, we used binary mixtures of 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) with [bmim⁺] based ionic liquids differing in size, shape and coordination ability of the anion ([bmim][BF₄], [bmim][N(CF₃SO₂)₂], [bmim][N(CN)₂], [bmim][SbF₆] and [bmim][CF₃SO₃]). Carbohydrate conversion in [bmim][BF₄]/[bmim][Cl] binary mixtures, has been studied under both magnetic stirring and ultrasound (US) activation. The catalytic system used led to the formation of 5-hydroxymethylfurfural in good yield under mild conditions. A significant influence of IL binary mixture composition on the outcome of the target processes was evidenced. Improvements in both reaction time and temperature have been observed, under US activation.

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1. Introduction

Energy demand in modern society and the negative consequences of global warming during the last decade have raised a growing interest in the scientific community toward renewable energy sources. In this scenario, the production of energy by means of solar cells or from bio-resources is an issue of paramount importance. In particular, as far as vegetable biomass is concerned, much attention has been paid to the production of industrially relevant intermediates from carbohydrates. These are a major component of biomass derived from wood processing by-products, agricultural surplus and so on. The dehydration of carbohydrates can give rise to important chemicals, such as furfural (FUR) and 5-hydroxymethylfurfural (5-HMF), which are currently obtained from petroleum manufacturing, and are used as starting materials for many industrial processes [1–7]. Thus, the implementation of carbohydrate conversion processes might have significant outcomes from both an economical and, most importantly, an environmental point of view.

The conversion of mono- and disaccharides into FUR and its derivatives has been widely investigated in both water [8–14] and conventional organic solvents [15–22]. Very recently, with the introduction of ionic liquids (ILs) as alternative reaction media, many studies have been directed toward the possibility to study these processes changing the nature of both the solvent media and the catalyst, or even varying other important operational parameters such as the reaction time and temperature dependence of different heating methods used [23–33]. Regarding this topic, different reports have analyzed the effect of microwaves on carbohydrate conversion [34–38]. On the other hand, US activation has been little investigated and it has been mostly applied only to improve carbohydrate dissolution in the solvent media used [39–42].

The use of ILs is advantageous because of their low flammability and possible reuse of the reaction media. Reports have highlighted that conversion of mono- and polysaccharides is favored in particular by chloride based ILs. Indeed, the high coordination ability of the chloride anion allows the formation of hydrogen bonds with the hydroxyl groups of the sugar units, favoring the dissolution of the substrate and, on the whole, its dehydration [43–45]. However, from a practical point of view the use of halide based ILs poses some limitations. As a matter of fact, these ILs are usually solid at room temperature and the liquid phases obtained on their melting show

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high viscosities. Consequently, high reaction temperatures have to be used in order to overcome these problems. This frequently causes the reaction mixture to turn brown, with the concomitant degradation of FUR and its derivatives into by-products of low industrial value. Furthermore, as the degradation processes of FUR are favored by water, an additional problem stems from the significant hygroscopicity of halide based ILs, making it difficult to carry out the target process in perfectly anhydrous media. From an environmental point of view, also the good water solubility and high thermal stability of halide based ILs pose some problems. Indeed, as a consequence of their possible release, the aqueous solubility might induce unwanted effects in aquatic ecosystems. On the other hand, the high thermal stability might favor their bioaccumulation [46–49].

Several attempts have been made to lower the viscosity of halide based ILs, and the use of conventional solvents/IL binary mixtures has been suggested [50]. However, this option could increase the environmental impact of the process. Therefore, to overcome the aforementioned problems, and bearing in mind the role played by chloride based ILs, we reasoned that the use of IL binary mixtures could be a valid alternative. Recent reports have highlighted some peculiar features of IL binary mixtures, which frequently show a strikingly different behavior with respect to the pure components, in particular as far as mixtures of anions are concerned [51–54]. Indeed, in the latter case, differences in size and coordination abilities of anions may give rise to either an ideal behavior or to a solvent system characterized by the presence of different micro-domains [55]. In this area, using the mononuclear rearrangement of heterocycles as a probe reaction, we have recently demonstrated that mixing of cations having significantly different electronic properties, induced a gradual change in the properties of the binary mixtures which perfectly reside between those corresponding to pure components. On the other hand, mixing anions differing in size, shape and coordination ability produced a discontinuous behavior, so that the properties of the binary mixtures obtained could not be related to the pure ILs [56].

In view of this, we studied on the conversion of carbohydrates into 5-HMF using IL binary mixtures such as [bmim][X]/[bmim][Cl], i.e. ILs all sharing the imidazolium cation, but differing in size, shape and coordination ability of the anion. This study was mainly aimed at identifying the most suitable co-solvent able to decrease the [bmim][Cl] viscosity, thus allowing the target process to be carried out close to room temperature. Fructose, glucose and sucrose were used as substrates (Scheme 1).

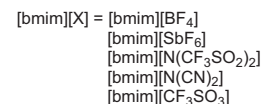
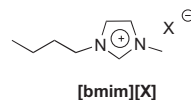
Carbohydrate conversion was carried out under acidic catalysis; in particular, we tested both species derived from renewable sources such as citric and tartaric acid, as well as strongly acidic resins differing in particles size, such as Amberlyst 15 and Dowex 50W X8 (hereafter indicated as Dowex). Reactions were initially carried out under magnetic stirring. However, taking into account that the sustainability of a process heavily depends on the amount of energy used, we also investigated the effect of US activation on the target processes, with the aim to decrease the reaction temperature and time.

2. Experimental

2.1. Materials

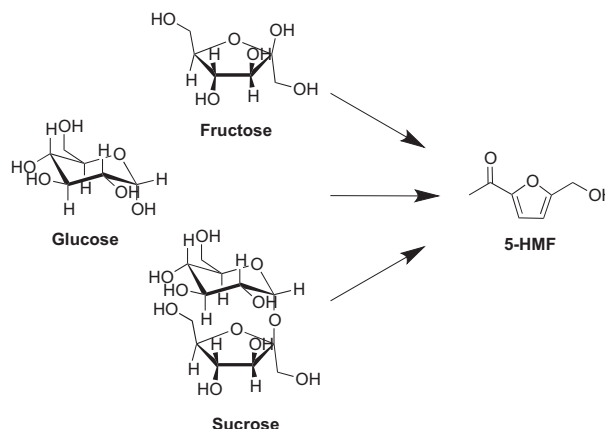
Fructose (≥ 99.0), glucose (≥ 99.5), sucrose (≥ 99.5), citric and tartaric acids (≥ 99.5) were purchased from Sigma–Aldrich and used without further purification. Amberlyst 15 (hydrogen form) and Dowex 50W X8 resins were purchased and kept before use overnight in a desiccator at 373 K, under vacuum and over phosphorus pentoxide.

ILs used:



X = Cl, BF₄, SbF₆, N(CF₃SO₂)₂, N(CN)₂, CF₃SO₃

The reactions studied:



Scheme 1. Schematic representation of ILs used and reactions studied.

[bmim][Cl], [bmim][BF₄] and [bmim][CF₃SO₃] were purchased from Iolitec. [bmim][N(CF₃SO₂)₂], [bmim][SbF₆] and [bmim][N(CN)₂] were prepared according to previously reported procedures [57–59]. Before use, all ILs were dried on a vacuum line at 343 K for 2 h, lyophilized for 48 h at 0.06 mbar, and stored in a desiccator under argon and over calcium chloride.

Each IL binary mixture was prepared by weighing the required amount of IL into a round bottom flask. To favor mixing, each mixture was vigorously stirred, sonicated for 1 min (45 kHz, 200 W) and then left to equilibrate overnight. In all cases the mixtures appeared to be homogeneous after this treatment.

2.2. General procedure for carbohydrate conversion under magnetic stirring

A suitable amount of carbohydrate (0.025 g) was weighed in a round bottom flask containing the pure IL or IL binary mixture (0.5 g). To favor carbohydrate dissolution, the mixture was stirred at 353 K for 30 min under argon. In all cases, the mixtures appeared to be homogeneous after this treatment. After equilibration at the reaction temperature, the suitable amount of acidic catalyst (0.025 g for fructose and glucose and 0.05 g for sucrose) was added. After reaction time, each sample was diluted with 0.250 g of ultra pure water, stirred at room temperature and diluted with methanol in such a way to have a 5-HMF concentration ranging from 7×10^{-6} M up to 7×10^{-5} M. The concentration of 5-HMF was determined from UV absorbance recorded at 277 nm. The presence of 5-HMF in the reaction mixture, as single UV absorbing product, was further verified by means of TLC on silica gel by comparison with a standard sample (eluent: ethyl acetate/methanol 5:1, v/v).

2.3. General procedure for carbohydrate conversion under US activation

Sonochemical reactions were carried out in a thermostated ultrasonic bath operating at a frequency of 45 kHz, with an output power of 200 W. The bath was filled with a 1% (w:w) aqueous solution of the surfactant Contrad 2000. Prior to each reaction

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