



# Isomeric distribution of monosaccharides in deep eutectic solvents: NMR study

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## ABSTRACT

As counter parts of ILs, DESs have received general interest because of their comparable physicochemical properties to ILs and facile preparation from readily available chemicals. In this work, the isomeric distributions of fructose, glucose, xylose and GlcNAc in CCU, CCG and CCO, i.e. basic, neutral and acidic DES, have been determined by <sup>13</sup>C NMR. Higher furanose fraction of fructose was observed in CCO compared to CCG and CCU. The glucose was chosen as model compound to reveal the effect of DES on the mutarotation behavior with DMSO *d*<sub>6</sub> as co-solvents. The experimental results showed that a high ratio of CCU to glucose speed up the mutarotation rate of glucose in DMSO *d*<sub>6</sub>, but have little influence on the anomeric distribution. Furthermore, the mutarotation of glucose in DESs is mainly driven by the HBD, whereas HBA provides little influence. However, HBD and HBA display a synergistic effect on the glucose mutarotation process. Hydrogen bonding between hydrogen of amino in urea and oxygen of hydroxyl in glucose is the driving force for the interconversion of anomers.

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## 1. Introduction

Ionic liquids (ILs) have attracted attention as green solvents to replace water and volatile organic solvents for conversion of carbohydrates to platform chemicals, such as 5-hydroxymethylfurfural (5-HMF) [1–3], furfural [4], and levulinic acid (LA) [5]. Major advantages are ILs unique properties such as high thermal stability, non-flammability, and good solvation [6]. However, the high prices and occasionally high melting temperatures for ionic liquids often limits their use as solvents for dehydration of hexoses (such as fructose [7], glucose, and glucosamine) and pentose (such as xylose [8]) to biofuel and bio-chemicals. Deep eutectic solvents (DESs), the counterpart of ILs, are mixtures of two organic components, which are capable of self-association generally through strong hydrogen bond interaction [9,10]. DESs share many similar physicochemical properties with ionic liquids [11]. As DESs show unique advantages compared to ionic liquids, making DES a promising solvent for biorefinery overcoming the limitations of ionic liquids. For example, the choline chloride (ChCl) based DESs are easier to prepare in large scale by heating or grinding without

tedious synthesis and purification steps [12]. Due to the low prices and nontoxicity of the starting materials, the prepared DESs are cheaper and most of them considered to be green, biodegradable and biocompatible [13,14]. Owing to the above advantages, dissolution [15], catalysis [16], material preparation [17], gas absorption [18,19] and separation [20,21], have been carried out in this novel reaction media recently.

Monosaccharide, such as glucose, xylose and *N*-acetyl-D-glucosamine (GlcNAc), are known to exist in two major forms in equilibrium, depending on the solvent (i.e.  $\alpha$ - and  $\beta$ -pyranoses, Fig. 1). However, fructose commonly presents more tautomer forms at equilibrium (Fig. 1). The isomeric distribution of monosaccharides has attracted significant interest because of their relevance to the mechanism of biomass transformation [22]. Especially, the distribution has an influence on product selectivity [23–25]. Nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy and molecular dynamics calculation have proved that 5-HMF is only derived from furanose tautomers ( $\alpha$ - and  $\beta$ -furanose), while side products, like humins, are from pyranose tautomers in dimethyl sulfoxide (DMSO) and polar solvents like 2,5-(dihydroxymethyl)-tetrahydrofuran (DHMTFH), tetrahydrofuran (THF) and tetrahydrofurfural alcohol (THFA) [23,25,26]. In another word, a high fraction of furanose forms in reaction media may lead to a higher 5-HMF yield and cleaner reactions. Our recent work show that fructose mainly exists as  $\beta$ -pyranose in ZnCl<sub>2</sub> molten salt

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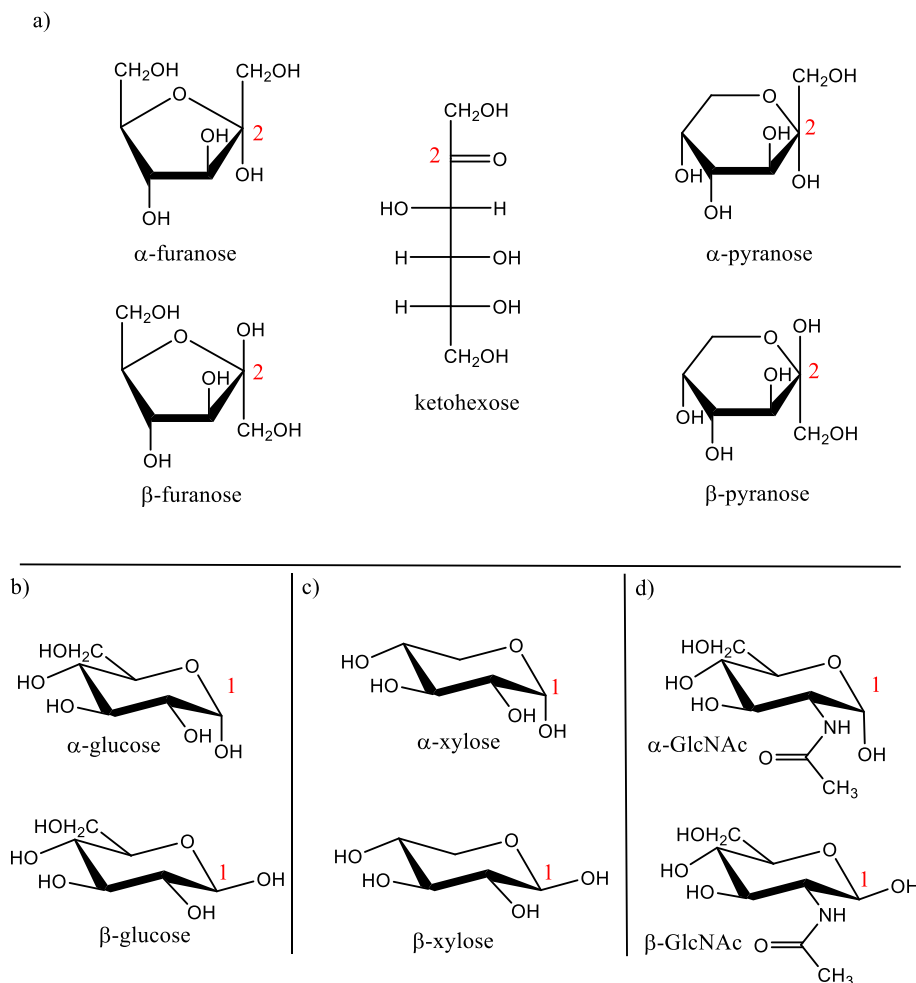


Fig. 1. Structures of studied monosaccharides a) fructose, b) glucose, c) xylose, d) GlcNAc.

hydrate, moreover, the relationship between tautomer distribution, reaction pathway and product selectivity in this reaction media was well established [27].

The isomeric distribution of monosaccharides, such as fructose, and its impact on the product has been noticed and studied in various solvents. However, it is still not been studied in DESs and in connection with biorefinery. For example, Han et al. examined various ChCl-based DESs as catalysts and solvents in conversion of fructose to the platform chemical 5-HMF, and compared it to the properties of ILs [3]. The DESs composed of Brønsted acids (like citric, oxalic or malonic acid) or Lewis acids (like  $\text{ZnCl}_2$  or  $\text{CrCl}_2$ ) and ChCl showed good solubility of fructose and the best one (ChCl and citric acid, 1:2) gives 76% yield of 5-HMF. Assanosi and co-workers reported the preparation of DES by ChCl and *p*-toluene sulfonic acid monohydrate (*p*-TSA) [28]. Applying this DES under the optimized reaction conditions, the 5-HMF yield reached up to 90.7%, owing to the stronger acidity of *p*-TSA. For pentose, Zhang et al. reported that xylose dehydration reactions were conducted in ChCl/citric acid with  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , and 54% furfural yield were obtained [29]. Although DESs have been developed as good reaction media for biorefinery, there are, as it comes to our knowledge, still no systematical studies of the isomeric distribution of monosaccharides in DESs. In order to study the mechanism of monosaccharides conversion in DESs, the correlation between the isomeric distribution and product selectivity need to be established. In order to optimize reaction condition and perform mechanistic studies this fundamental, but crucial knowledge, should be obtained.

NMR spectroscopy is an ideal and precise tool to evaluate the isomeric distribution of monosaccharides [30–32] and component analysis

[33]. However, the viscosity of DESs distorts the  $^1\text{H}$  NMR spectra and the signals from the anomeric protons cannot be well resolved. Fortunately, the lower resolution and overlap signals in  $^1\text{H}$  NMR, could be overcome by using quantitative  $^{13}\text{C}$  NMR [31]. To ensure the quantitative reliability of  $^{13}\text{C}$  NMR spectra, it is common to set an excessive relaxation delay at least 10 times as long as the longest  $T_1$  value, which allow complete relaxation of each carbon atom of monosaccharides.

In this study, we evaluate the isomeric distribution of fructose, glucose, xylose and GlcNAc in basic, neutral and acidic DESs, ChCl-urea (CCU), ChCl-glycerol (CCG) and ChCl-oxalic acid (CCO) by  $^{13}\text{C}$  NMR at 303 K at equilibrium. Besides, the effect of DES concentration on the mutarotation the roles of hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) were clarified, using DMSO  $d_6$  as the co-solvent. The hydrogen bonding interaction between the HBD of DESs and the monosaccharides is a major driving force for mutarotation. To the best of our knowledge, this is the first study of the isomeric distribution of sugars in DESs systems.

## 2. Experimental section

### 2.1. Materials

Fructose (analytical grade, 99.8%), glucose (analytical grade, 99.5%) and xylose (analytical grade, 99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. GlcNAc (analytical grade) was obtained from Golden-Shell Biochemical Co., Ltd.  $^{13}\text{C}$ -labeled glucose, ChCl (analytical grade), *N,N'*-dimethylurea (DMU) (analytical grade), tetramethylurea (TMU) (analytical grade) and sodium 2,2-dimethyl-

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