Solubility of glucose, xylose, fructose and galactose in ionic liquids: Experimental and theoretical studies using a continuum solvation model

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ABSTRACT

A molecular screening of 64 ionic liquids (IL's) for the solubility of monosaccharides such as D-(+)-Glucose, D-(+)-Xylose, D-(−)-Fructose and D-(+)-Galactose were performed by continuum solvation model (COSMO-RS) over the temperature range of 303.15–373.15 K. The IL data set consisted of 31 cations and 23 anions comprising of cations such as imidazolium, ammonium, pyridinium, pyrrolidinium, phosphonium, sulfonium and piperidinium. The imidazolium and ammonium based IL's gave the highest solubility for cations possessing lesser number of carbon side chains. Based on the screening studies, the following two IL's were chosen: 1-ethyl-3-methylimidazolium thiocyanate ([EMIM][SCN]) and Tris(2-hydroxyethyl)methyl ammonium methylsulfate [TMA][MeSO$_4$] to experimentally study the solubility of monosaccharides in the two IL's. The experimentally obtained solid–liquid equilibria (SLE) values were then compared with COSMO-RS predicted values. The root mean square error (RMSE) values of monosaccharides such as D-(+)-Glucose, D-(+)-Xylose, D-(−)-Fructose and D-(+)-Galactose in [EMIM][SCN] were 3.11%, 3.12%, 2.32% and 1.83% respectively while the corresponding figures in [TMA][MeSO$_4$] is 1.47%, 1.20%, 2.94% and 0.70%. The overall solubility ranking in two IL's was: D-(−)-Fructose > D-(+)-Xylose > D-(+)-Glucose > D-(+)-Galactose.

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1. Introduction

The perpetual population growth has pushed towards an increased utilization of fossil fuels in the production of energy and chemicals [1]. However the changes made to harness the fossil resources have made more impact on the economic and environmental processes. This has led to an increase in the production of CO_2 in the environment. An alternative approach for this problem is in the form of lignocellulosic biomass as a suitable energy source of the future [2,3]. For the management and maintenance of natural resources, Agenda 21 has been initiated which aims to decrease the fossil resources and non-renewable resources (petroleum, natural gas, coal and minerals) [4]. Biomass is a source of fuels, environmentally favorable and the most abundant renewable biological raw material of the earth. Currently lot of research is carried out which deals with the conversion of lignocellulosic biomass to value added chemicals [5,6]. According

to statistics, the entire energy produced from photosynthesis is ten times higher than that of fossil fuel resource used in the world every year [7].

Biomass is the carbon based material composed of organic molecules containing carbon and hydrogen. The carbon used to construct the biomass is absorbed from the atmospheric CO_2 by the plant life using the energy from sunlight. The major components of lignocellulosic biomass are cellulose (30–50%), hemicellulose (20–35%) and lignin (5–30%)). Some of the sources of biomass are the waste agriculture residue, wood, grass, forestry and municipal solid wastes [8–12]. The biomass conversion processes include set of chemical and biological processes, including separation, fermentation reactions, conversion of biopolymers into other valuable products and pre-treatment of biomass [13]. All together these processes require suitable solvents for the dissolution of biomass based components [14]. Biomass is hard to dissolve in common organic solvents due to their complex structure and strong intra–inter molecular hydrogen bonding [7]. Ionic liquids (ILs) are suitable solvents in the biorefining processes, because ILs exhibits several attractive properties such as those of solvent and also performs as a catalyst for some reactions. The advantage of IL's in these processes is that it can dissolve whole biomass or selective polysaccharides such as cellulose, hemicellulose and lignin. The hydrolysis of

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polysaccharides further gives us reducing sugars. IL's have reported to be efficient solvents for the dissolution of carbohydrates [15]. This is important as a small change in cation or anion structure, results in the large difference in the physical and chemical properties such as density, viscosity and chemical affinity with other compounds [15].

There has been recent work which reports the solubility of carbohydrates in IL's. Carneiro et al. [2] measured the solubility of xylitol and sorbitol in three IL's at a temperature range of 10–60 °C. Sorbitol showed a slightly higher solubility than xylitol. Both sugars showed high solubility for [EMIM][EtSO₄] as compared to aliquat336 and aliquat [NO₃]. Liu et al. [16] determined the solubility of glucose in IL + anti solvent mixtures at temperature of 0–60 °C. [EMIM][Br] gave the highest solubility as compared to [BMIM][Cl], [HMIM][HSO₄], [BMIM][Ac] and [EMIM][Ac]. Carneiro et al. [1] using HPLC technique, experimentally measured the solubility of glucose and fructose in ILs. Domanska and co-workers [17], investigated the solubility of sugar alcohols in the dicyanamide based ionic liquids namely [BMIM][DCA], [BMPyr][DCA], and [BMP][DCA] by experimental and PC-SAFT modelling over the temperature range of 293.15–363.15 K. The sugar alcohols, xylitol and sorbitol have been considered for their solubility study. The measured solubility data of xylitol and sorbitol have shown satisfactory results with PC-SAFT predicted data.

Thus in order to study the solvation property, the solubility data of IL's in biomass components are a prerequisite for the design of separation and reaction units [18–24]. Further when ILs are used as solvents, there is also a possibility for its regeneration and reutilization which ultimately reduces the associated process cost [25]. Thermodynamic models such as non-random two liquid (NRTL) and UNIversal QUASi-Chemical theory (UNIQUAC) are generally used to describe and predict the phase equilibria of the mixture (solid–liquid equilibria) containing monosaccharides and IL [26–31]. However both NRTL and UNIQUAC model are dependent on experimental data for generating the binary interaction parameters. Data for new functional groups involving IL's and monosaccharides are missing which leads to the application of UNIFAC model too defunct. Quantum chemical based solvation model such as COSMO-RS is an alternative for such systems [32,33]. It requires only the universal parameters and component specific parameters [34,35] fitted with a small experimental data set. COSMO-RS requires chemical structure of the component as the only information [36,37]. By COSMO-RS model; we can predict the solubility of any component in the mixture (solid–liquid equilibria). This model can be used to calculate the infinite dilution activity coefficient of any solute in solvent [17,38,39]. Thus the SLE calculation merely requires the melting point temperature and heat of fusion values of the solute which is monosaccharides in our case.

Thus in this study, initially a molecular screening of 64 IL's for the solubility of monosaccharides such as D-(+)-Glucose, D-(+)-Xylose, D-(−)-Fructose and D-(+)-Galactose were performed by COSMO-RS model over the temperature range of 303.15–373.15 K. The IL data set consisted of 31 cations and 23 anions comprising of cations such as imidazolium, ammonium, pyridinium, pyrrolidinium, phosphonium, sulfonium and piperidinium. Based on the screening studies, the following two IL's were chosen: 1-ethyl-3-methylimidazolium thiocyanate ([EMIM][SCN]) and Tris(2-hydroxyethyl)methyl ammonium methylsulfate [TMA][MeSO₄] to study the experimental solubility of monosaccharides in IL's at a temperature range 303.15–373.15 K. Further the apparent standard thermodynamic function of dissolution such as standard molar Gibbs energy $\Delta_{dissol.}^{o}G$, molar enthalpy $\Delta_{dissol.}^{o}H$ and standard molar entropy $\Delta_{dissol.}^{o}S$ were also calculated from the modified van't Hoff equation.

2. Computational details

2.1. Geometry optimization

The initial structures of selected monosaccharides and IL's were drawn in the MOLDEN freeware software [40]. Particular attention has been paid for the selection of the cation and anion. IL's having melting point less than the room temperature was chosen in COSMO-RS studies. The structures of all IL's are depicted in the Supplementary information (Table S1). The melting properties (melting temperature and heat of fusion) of monosaccharides are reported in Table 1, which are used in the COSMO-RS (solid–liquid equilibria) Prediction. The initial molecular geometries were fully optimized by HF/6-31G* via Gaussian03 package [41–43]. To detect the presence of any negative or imaginary frequencies, frequency optimization was done using the *freq* keyword in Gaussian03 [44].

After the geometry optimization step, the next step is to generate the COSMO file using the final optimized structure. The first step of COSMO-RS calculation is to estimate the sigma profiles (i.e., the screening charge densities) of each species [45]. The equilibrium geometry of the molecules in the ideal gas phase was first obtained using the density functional theory of P BV86 [6,46]. The triple zeta valance potential (TZVP) basis set was then used in combination with the density fitting basis set of DGA1 [42,47,48]. The combination of TZVP and DGA1 basis sets allows the electron density to adjust spatially to the extent appropriate to the particular molecular environment. The ideal screening charges on the molecular surface were then computed using the same level of theory P BV86 via the keyword "scrf = COSMORS". The default radii of the elements as used in Gaussian03 for the keyword "scrf = COSMORS" were used to define the cavity for the molecule [49,50].

The physical parameters such as $a_{eff} = 632\,\text{Å}^2$ (surface area of a standard segment), $\alpha' = 8419\,(\text{K cal Å}^4)/(\text{mol. e}^2)$ (misfit constant for misfit energy interaction), $c_{hb} = 75006\,(\text{K cal Å}^2)/(\text{mol. e}^2)$ (constant for hydrogen bonding interaction) and $\sigma_{hb} = 0.0084\,\text{e}/\text{Å}^2$ (the cut off value for hydrogen bonding interactions) were taken from the work of Balaji et al. [6] and were not modified in our calculations.

We have assumed a complete dissociation of ILs into cations and anions with equi-molar quantities. The sigma profile of the ionic liquid is the linear addition of the sigma profiles of the cation and anion (Eq. (1)):

$$p_{\text{ionic liquid}}(\sigma) = p_{\text{cation}}(\sigma) + p_{\text{anion}}(\sigma) \qquad (1)$$

where $p_{\text{cation}}(\sigma)$ and $p_{\text{anion}}(\sigma)$ are the sigma profiles for cation and anion respectively. We have obtained the sigma profile of cation and anion separately and then added them up by simple algebraic addition. After the addition the sigma profile have been normalized. Thus profile will behave as a profile of single molecule [6]. This is equivalent to calculating the sigma profile of a mixture of cation and anion. Along with the sigma profile, the COSMO volume (i.e., the cavity surface volume) and area (cavity surface area) also get added linearly. Thus an independent ion model has been used in this work.

Table 1
Melting point and heat of fusion of monosaccharides used in this work.

Solute	Chem. formula	M (g mol⁻¹)	T_{fus} (K)	$\Delta_{fus}H$ (J mol⁻¹)	Ref.
D-(+)-Glucose	$C_6H_{12}O_6$	180.2	431.15	32220	[13,59]
D-(+)-Xylose	$C_5H_{10}O_5$	150.1	416.15	31700	[13]
D-(−)-Fructose	$C_6H_{12}O_6$	180.2	378.15	26000	[13]
D-(+)-Galactose	$C_6H_{12}O_6$	180.2	443.15	43740	[13,59]