Fluid Phase Equilibria 448 (2017) 168–177

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Solubility of glucose in tetrabutylammonium bromide based deep eutectic solvents: Experimental and molecular dynamic simulations

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ARTICLE INFO

Article history:
Received 3 February 2017
Received in revised form
26 May 2017
Accepted 28 May 2017
Available online 1 June 2017

Keywords:
Deep eutectic solvents
Glucose
Isomerization
Molecular dynamics
Solubility
Thermodynamic models

ABSTRACT

The present work attempts to measure the solid-liquid equilibrium (SLE) of glucose in three novel low cost deep eutectic solvents (DES) namely tetrabutylammonium bromide [TBAB]-Imidazole, [TBAB]-ethylene glycol, and [TBAB]-glycerol over the temperature ranging from 299.15–353.15 K. The [TBAB]-Imidazole DES gave the highest solubility of glucose in among all the DES. The experimental solubility data was correlated with the Apelblat empirical equation along with regression using local composition models namely NRTL and UNIQUAC models. The thermodynamic functions of dissolution such as enthalpy $\Delta^{o}_{dissol}H$, Gibbs energy $\Delta^{o}_{dissol}G$ and entropy of dissolution $\Delta^{o}_{dissol}S$ were also calculated from the modified van't Hoff equation. The dissolution functions gave positive values for all the studied systems indicating that the process is endothermic in nature while being non-spontaneous and entropically favourable. In addition, classical Molecular Dynamic (MD) simulations were performed to disclose the glucose-DES interactions. From MD simulations, the anion and hydrogen bond donor (HBD) molecules is seen to overall dominate the dissolution of glucose. The anion of hydrogen bond acceptor (HBA) and the HBD molecules are primarily responsible for the dissolution of glucose. The isomerization of glucose to fructose in [TBAB]-Imidazolium DES was observed for temperatures above 313.15 K, which resulted in a lower concentration of glucose at higher temperatures.

1. Introduction

In the present scenario, high utilization of fossil fuels have made a significant impact on the environment which includes increased co-production of hazardous chemicals [1]. This has led to an enhanced carbon dioxide production. An alternative pathway for this problem is the use of cheap and environmental friendly feedstock such as lignocellulosic biomass. These are suitable feedstock for the production of energy and chemicals of the future [2,3]. Lignocellulosic biomass is a complex assembly of cellulose, hemicellulose and lignin and depending on the source of biomass, species can be of *circa* or 35–50 wt% of cellulose, 15–30 wt% of hemicellulose, 18–30 wt% of lignin, and 2–5 wt% of other compounds [4].

Cellulose is the most abundant biopolymer on the earth and a major component in the lignocellulosic biomass [5]. The carbohydrate D-glucose, a hexopyranose with two stereoisomers (i.e., α-D-glucopyranose and β-D-glucopyranose), is the monomer of cellulose. D-glucose is an indispensable compound which is involved in various biological functions and are important renewable feedstock in the production of biofuels [6,7]. The major goal of second generation biofuel production is to recover these cellulose from wood and then proceed it towards a pathway for hydrolysis in order to obtain glucose. This upon fermentation produces bioethanol [8–10]. Several alternative processes exists for the separation of cellulose from wood [9,10]. It is a well-known fact that common solvents such as water are not able to dissolve the cellulose at lower operating conditions as it requires higher operating temperature and pressure to dissolve cellulose [11]. Therefore, it necessitates the use of other solvents. On the other hand, the common organic solvents namely dimethylacetamide/lithium chloride, N_2O_4-N, $LiClO_4\cdot 3H_2O$, $LiSCN\cdot 2H_2O$ and N-methylmorpholine-N-oxide/H_2O are also used for the dissolution of cellulose [12–14]. However, these solvents are volatile in nature and are toxic, expensive and requires higher operating conditions. They are also very difficult to recover as it demands higher temperatures,

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http://dx.doi.org/10.1016/j.fluid.2017.05.024

and uncontrollable side reactions [15].

Among several alternatives being investigated as a solvent for the cellulose, Ionic Liquids (ILs) are found to be good candidates for the dissolution of cellulose [5,16]. During past few decades, ILs are promising solvents for the dissolution of lignocellulosic biomass and its components [10,17]. A good fraction of ILs are considered as green solvents owing to their several attractive properties such as negligible vapour pressure, non-toxic, non-flammability and high thermal and chemical stability [16,18,19]. However, ILs are also not free from constraints such as high cost, complexity in synthesis and controversial environmental acceptability [20,21]. Hence in recent years, the use of new class of green solvents namely Deep Eutectic Solvents (DES) are being explored [22].

A good solvent should possess low melting temperature, less viscosity and further should not be non-toxic and non-corrosive in nature. DES exhibits several attractive properties similar to ILs *i.e.,* high thermal and chemical stability, non-flammability and negligible vapour pressure. Additionally a higher proportion of newly prepared DESs are liquid at room temperature [22,23]. DES are formed by low cost precursors, where it is prepared by the association of a hydrogen bond acceptor (HBA) which is a Lewis acid and a hydrogen bond donor (HBD) possessing an extra lone pair of electron [24]. These constituents are mixed in specific proportion to produce a molten mixture upon heating which then slowly transforms to a liquid phase at or near room temperature. The preparation of DES is also less complex and economical when compared with ILs [25,26]. It should be also easy to store, possess high chemical and thermal stability and most importantly should not degrade the lignocellulosic monomers [7,10]. Over the last few decades, there are extensive investigations carried out on the dissolution of cellulose, wood, lignin and carbohydrates in IL and organic solvents by both computational (COSMO-RS, Molecular Dynamics (MD), Quantum Chemical (QC)) and experimental studies [10,27–30]. Therefore it necessitates the exploration of these solvents for the dissolution of carbohydrates [31].

Till date the dissolution of monosaccharides, disaccharides and sugar alcohols have been extensively studied in ILs and organic solvents [19,32–35]. Contrary to ILs and organic solvents, the solubility data for carbohydrates in DES are scarce. Thus, the present study is to report the solubility of glucose in the three prepared DES namely tetrabutylammonium bromide [TBAB]-Imidazole, [TBAB]-ethylene glycol, and [TBAB]-glycerol. The solubility of glucose will then be measured over the temperature range from 299.15 to 353.15 K. Furthermore, MD simulations will be attempted for the glucose-DES system to understand the microscopic insight into the molecular interactions. This will be complemented by radial distribution functions (RDF) and non-bonded interaction energies of the respective system(s). On the macroscopic front, the apparent standard thermodynamic functions of dissolutions will also be calculated from the modified van't Hoff equation. Finally the Gibb's free energy models (Non-Random Two Liquid (NRTL) and UNIversal QUAsi-Chemical theory (UNIQUAC)) will be used to describe and predict the phase equilibria of glucose mixtures.

2. Computational details

2.1. Molecular dynamic simulation

Initially, the chemical structures of all the studied molecules were drawn by Avogadro freeware [36]. The respective molecular geometries were optimized by *Gaussian09* program using the B3LYP/6-311 + G* level of theory [37]. Partial charges were obtained by restrained electrostatic potential (RESP) charge derivation method [38]. For all the molecules, the generalized AMBER force field (GAFF) parameters were employed [39]. The generalized AMBER force field parameters were developed by using *Antechamber* [40]. Fig. 1 shows the chemical structures of glucose, salt and hydrogen bond donors with atom notations. The developed force field parameters were confirmed by measuring the density of DES, hydrogen bond donor molecules at 298.15 K. The experimental and simulated densities gave an excellent agreement as evident from Table 1. The detailed description of experimental measured density was given in supporting information.

All the MD simulations were performed with the NAMD version 2.10 [41] at constant temperature (298.15 K) and atmospheric pressure using Langevin thermostat and Nose-Hoover Langevin barostat [42,43]. The SHAKE algorithm was adopted to constrain the lengths of all covalent bonds to hydrogen [44]. The Ewald summation method was applied to treat the long-range electrostatic interactions at the cut-off distance of 12 Å. The time step was kept at 1 fs [45]. We have disabled the Particle Mesh Ewald (PME) grid size and used only *PMEGridspacing*. This uses a grid spacing value of 1 Å. Thereafter NAMD calculates the grid size automatically based on the grid spacing and the cell size values. The initial configuration of glucose-DES are prepared by PACKMOL in a cubic box with a random distribution of molecules [46]. The size of the cubic box was typically larger than the actual box size which makes the packing easier. For the MD simulation system, 26 molecules of glucose and 200 molecules of DES gave a glucose mole fraction of 0.115 and DES 0.885. Within the mole fraction of DES, the individual mole fraction of DES constituents for [TBAB]-Imidazole was 0.295 of salt [TBAB] and 0.59 for imidazole. Here, the ratio of HBA to HBD is 1:2 (0.295/0.595). For the other two DES, [TBAB]-glycerol and [TBAB]-ethylene glycol the molar ratio among HBA to HBD is 1:4. Thus, the salt ([TBAB] or HBA) mole fraction was 0.177, while it was 0.708 of HBD or ethylene glycol/glycerol. So for MD studies involving [TBAB]-Imidazole, 200 molecules of [TBAB] was mixed with 400 molecules of imidazole. Similarly, 200 molecules of salt [TBAB] was mixed with 800 molecules of glycerol or ethylene glycol.

Initially, the system energy was minimized for 1 ns and then gradually heated to desired temperature for 0.5 ns. At the desired temperature, the system was equilibrated for 8 ns under NPT ensemble to get the system converge to its experimental condition. Here, the simulated density is compared with the measured density to confirm its convergence to the experimental condition. From Fig. S1, it can be seen that the volume of the simulated system is constant for last 2.5 ns i.e., 5.5–8 ns. From this constant simulated volume, simulated density can be calculated and compared with measured density and with it we come to know the final volume of the system for the production run. Subsequently, the production run was executed for 25 ns under NPT ensemble. At every 5 ps, the production data was saved for structural analysis from the simulated trajectories using VMD software [47]. Three Random Structure of DES-Glucose have been studied for each simulation condition with the average values of analysed properties reported here. In the mixture of glucose-DES, the interaction energy and hydrogen bonds between DES and glucose are calculated per mole of glucose.

3. Materials and methods

3.1. Materials

Tetrabutylammonium bromide ([TBAB]) and Imidazole having purity ≥99% was purchased from SRL, India. Ethylene glycol and glycerol of purity ≥98% were purchased from Merck, India. The glucose (≥99.5%) was supplied by Sigma-Aldrich, Germany. These chemicals were of analytical grade and are used without further purification. The details of the chemicals used are given in Table 2.