



# Solvation behaviour and partial molar properties of monosaccharides in aqueous protic ionic liquid solutions



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## ARTICLE INFO

### Article history:

Received 19 October 2013  
Received in revised form 14 November 2013  
Accepted 15 November 2013  
Available online 25 November 2013

### Keywords:

Protic ionic liquid  
Monosaccharide  
3-Hydroxypropylammonium formate  
Density  
Speed of sound

## ABSTRACT

The densities,  $\rho$  and speeds of sound,  $u$  of D(+)-glucose and D(–)-ribose in water and in (0.10, 0.20, 0.30, and 0.40) mol · kg<sup>–1</sup> aqueous protic ionic liquid (3-hydroxy propylammonium formate) solutions were measured at temperatures,  $T = (298.15 \text{ to } 318.15) \text{ K}$ . Infinite dilution standard partial molar volume,  $V_2^\infty$  and standard partial molar isentropic compressibility,  $K_{s,2}^\infty$  have been calculated, which were used to evaluate the standard transfer volumes,  $\Delta_t V_2^\infty$  and  $\Delta_t K_{s,2}^\infty$ . The  $\Delta_t V_2^\infty$  and  $\Delta_t K_{s,2}^\infty$  values for monosaccharides decrease in the order: D(+)-glucose > D(–)-ribose. The transfer parameters are positive and increase with molalities of ionic liquid (IL) and with temperature. Further, the expansion coefficients,  $(\partial V_2^\infty / \partial T)_P$ , its derivative  $(\partial^2 V_2^\infty / \partial T^2)_P$ , pair ( $V_{AB}$  and  $K_{AB}$ ) and triplet ( $V_{ABB}$  and  $K_{ABB}$ ) volumetric interaction coefficients and hydration numbers,  $N_w$  have also been calculated and used to discuss the solvation behaviour of monosaccharides. The variation in the taste quality of monosaccharides in the presence of IL has also been studied from apparent massic volume,  $v_\phi$  and apparent massic isentropic compressibility,  $K_{\phi,m}$  parameters.

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## 1. Introduction

Due to the growing need for alternate renewable resources to diminishing fossil fuels, biomass is regarded as the most suitable and readily available substitute. The search for better conversion of biomass into fuels; biodegradable plastics and biocompatible composites and other materials have now attracted both industry and academia. Out of total annual renewable biomass produced by nature, 75% can be assigned to carbohydrates. Among these the most abundant natural polymer is cellulose and thus it represents the most desirable material for producing biocomposites [1–6]. But, due to the low solubility of cellulose, various aqueous and non-aqueous solvents have been used for its dissolution.

The use of traditional, expensive and uncommon solvents under harsh condition for cellulose dissolution processes, faces the challenge of recovering these solvents, which is one of the major hurdle in this field [3,7,8]. However, Swatoski et al. [9] reported the use of ionic liquids (ILs) as solvent for both the regeneration and chemical modification of the cellulose. Ionic liquids are novel class of green benign solvents, which promise wide-spread application in industry, possibly replacing currently used volatile organic solvents, due to their unique physicochemical properties [10].

Ionic liquids are considerably good solvents and capable of dissolving various polar and non-polar compounds. Thermophysical properties and behaviour of ILs with respect to their miscibility with other solvents or substrates can be regulated either by changing the chemical nature of the cation or that of the anion [11–15]. Choi and Kwon [16] used hydroxyethylammonium based protic ionic liquids (PILs) for the dissolution zein, an industrially important natural polymer. Some polymers such as polyaniline and polypyrrole are insoluble in many organic solvents, but found to be easily soluble in PILs [17]. The effect of the hydroxyl (–OH) group in PILs for the solvation with polar solvents has been revealed by the determination of solvato-chromic parameter [18]. PILs also offer a unique opportunity to study saccharide structure and properties using modern spectroscopic and analytical methods [9,19]. Saccharides being essential components of living systems play a key role in various aspects of chemistry, biochemistry, and technology. They are involved various processes such as cell–cell recognition, structure preservation and cell protection and are of technological use in the design of biodegradable biocompatible materials [20].

A number of literature reports [4–6] are available on the dissolution of cellulose in ILs but only limited studies [21–25] are present for low molar mass saccharides. In order to design a greener and efficient route for the transformation of biomass (cellulose) into fuels or other important chemicals, there is a demand to study the interactions between the monomer units of polysaccharide (cellulose) and ionic liquids. So, it was planned to study the

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physicochemical properties of D(+)-glucose and D(–)-ribose in  $m_B$  (molality of 3-hydroxypropylammonium formate) = (0.10, 0.20, 0.30, and 0.40) mol · kg<sup>-1</sup> aqueous solutions of 3-hydroxypropylammonium formate (3-HPAF) at temperatures,  $T$  = (298.15, 303.15, 308.15, 313.15 and 318.15) K. The various parameters evaluated from these studies are helpful to better understand the interactions between saccharide and protic ionic liquid.

## 2. Experimental

### 2.1. Materials

The provenance and purity of the chemical used are given in table 1. The monosaccharides were used as such after drying over anhydrous CaCl<sub>2</sub> in a vacuum desiccator for 48 h at room temperature. For the synthesis of IL, the 3-amino-1-propanol and formic acid were used without further purification.

### 2.2. Synthesis and characterization of 3-hydroxypropylammonium formate (protic ionic liquid)

The 3-hydroxypropylammonium formate (protic ionic liquid) was synthesized [17] by exothermic neutralisation of equimolar 3-amino-1-propanol with formic acid. The formic acid was added drop wise into 3-amino-1-propanol (base) in a two necked round bottom flask (fitted with dropping funnel and condenser) under vigorous stirring at a temperature below 283.15 K. After the complete addition, the reaction mixture was then continuously stirred for 24 h at room temperature. The resulting product obtained as viscous liquid was then dried at room temperature under high vacuum for two days, in order to remove moisture and excess of amine. This synthesized protic ionic liquid was further stored under N<sub>2</sub> atmosphere.

The proton NMR of 3-HPAF was recorded on Bruker Avance 500 MHz spectrometer using deuterated DMSO as solvent and TMS as the internal standard. For 3-HPAF, <sup>1</sup>H NMR {(DMSO,  $\delta \cdot 10^{-6}$ ):  $\delta = 8.43 \cdot 10^{-6}$  (s, 1H, HCOO<sup>-</sup>),  $\delta = 6.15 \cdot 10^{-6}$  (broad, 4H, OH and NH<sub>3</sub><sup>+</sup>),  $\delta = 3.45 \cdot 10^{-6}$  (t, 2H, CH<sub>2</sub>-N),  $\delta = 2.77 \cdot 10^{-6}$  (t, 2H, CH<sub>2</sub>-O),  $\delta = 1.65 \cdot 10^{-6}$  (qn, 2H, CH<sub>2</sub>-C)}. IR spectra were recorded on JASCO FT/IR- 4100 spectrometer, having maximum resolution of 0.9 cm<sup>-1</sup> and the signal to noise ratio of 22000:1. The broad band appeared in the range (3600 to 2600) cm<sup>-1</sup> exhibits the characteristic ammonium peak,  $\nu$ (N–H) and  $\nu$ (O–H) stretching vibration. The broad band centred around 1600 cm<sup>-1</sup> corresponds to the characteristic carbonyl,  $\nu$ (C=O) stretching and  $\delta$ (N–H) plane bending, vibrations. The water content of synthesized 3-HPAF ( $\approx 7124 \cdot 10^{-6}$ ) was measured by using Analab Karl Fischer Titrator (Micro AquaCal00).

### 2.3. Apparatus and procedure

The density  $\rho$  and speed of sound  $u$  of solutions were measured simultaneously by using a vibrating-tube digital density metre and sound velocity analyser (Anton Paar, DSA 5000 M). The two-in-one instrument is equipped with a density cell and a sound velocity

cell. Both cells are temperature controlled by a built-in Peltier thermostat (PT-100) having an accuracy of  $\pm 0.01$  K. The density metre was calibrated by Millipore, degassed water and dry air at atmospheric pressure. The uncertainty in the measurement of density and speed of sound is  $\pm 5 \cdot 10^{-3}$  kg · m<sup>-3</sup> and  $\pm 0.01$  m · s<sup>-1</sup>, respectively.

The solutions were made fresh on mass basis in air tight glass vials by using Sartorius balance (Model CPA225D) with a precision of  $\pm 0.01$  mg. All the solutions were made in Millipore quality freshly degassed water.

## 3. Results and discussion

The density  $\rho$  and speed of sound data  $u$  were used to calculate the corresponding apparent molar volumes,  $V_{2,\phi}$  and apparent molar isentropic compressibility,  $K_{s,2,\phi}$  of monosaccharides (D(+)-glucose and D(–)-ribose) in water and in  $m_B$  = (0.10, 0.20, 0.30, and 0.40) mol · kg<sup>-1</sup> aqueous 3-hydroxypropylammonium formate solutions at  $T$  = (298.15, 303.15, 308.15, 313.15, and 318.15) K by using equations:

$$V_{2,\phi} = [M/\rho] - [(\rho - \rho_o)/(m \cdot \rho \cdot \rho_o)], \quad (1)$$

$$K_{s,2,\phi} = (\kappa_s \cdot M/\rho) - [(\kappa_s^o \cdot \rho - \kappa_s \cdot \rho_o)/(m \cdot \rho \cdot \rho_o)], \quad (2)$$

where  $M$  and  $m$  are respectively, the molar mass and molality of the solute (monosaccharide);  $\rho$  and  $\rho_o$  are the densities of solution and solvent (water or water + 3-HPAF),  $\kappa_s$  and  $\kappa_s^o$  are the isentropic compressibilities of solution and solvent, respectively. Values of the isentropic compressibility,  $\kappa_s$ , were evaluated from the measured density  $\rho$  and speed of sound,  $u$  data as:

$$\kappa_s = 1/u^2 \cdot \rho. \quad (3)$$

The  $\rho$ ,  $V_{2,\phi}$ ,  $u$  and  $K_{s,2,\phi}$  results are given in table 2. The standard uncertainty in the determined  $V_{2,\phi}$  values resulting from the experimentally measured quantities ( $u(m) = 9.1 \cdot 10^{-6}$  mol · kg<sup>-1</sup>,  $u(\rho) = 5.0 \cdot 10^{-3}$  kg · m<sup>-3</sup>,  $u(T) = 0.01$  K) ranges from (0.09 to 0.030)  $10^6 \cdot m^3 \cdot mol^{-1}$  at ( $\leq 0.05$  mol · kg<sup>-1</sup>) and high concentration ranges of the saccharides, respectively and the standard uncertainties in  $K_{s,2,\phi}$  values ranges (0.80 to 0.40)  $10^{-15} \cdot m^3 \cdot mol^{-1} \cdot Pa^{-1}$  at ( $\leq 0.05$  mol · kg<sup>-1</sup>) and high concentration ranges of the saccharides, respectively. The  $V_{2,\phi}$  and  $K_{s,2,\phi}$  values of monosaccharides in water and in aqueous solutions of 3-HPAF increases with increase in concentration of monosaccharides as well as with temperature. A representative plot for the variation of  $V_{2,\phi}$  with solute (D(–)-ribose) concentration and temperature is depicted in figure 1. The  $V_{2,\phi}$  values increase on going from dark blue region of the curve to dark orange region.

The standard partial molar volumes at infinite dilution, ( $V_2^\infty = V_{2,\phi}^\infty$ ) and standard partial molar isentropic compressibility at infinite dilution, ( $K_{s,2}^\infty = K_{s,2,\phi}^\infty$ ) have been evaluated by least-squares fitting to the corresponding data as:

$$V_{2,\phi} = V_2^\infty + S_v \cdot m, \quad (4)$$

$$K_{s,2,\phi} = K_{s,2}^\infty + S_K \cdot m, \quad (5)$$

where  $S_v$  and  $S_K$  represent the respective experimental slopes. The  $V_2^\infty$  and  $K_{s,2}^\infty$  values of D(+)-glucose and D(–)-ribose in water and their comparison with literature values [26–37] have been given in tables 3 and 4. The  $V_2^\infty$  values of monosaccharides increase with concentration of IL and temperature, which indicate an increase in interactions between ions of 3-HPAF ( $-NH_3^+$ ,  $HCOO^-$ ) and saccharides, which may be due to the dominance of (hydrophilic + ionic) interactions. The magnitude of  $K_{s,2}^\infty$  values are negative in water as well as in aqueous solutions of 3-HPAF. Further,  $K_{s,2}^\infty$  values of saccharides increase with IL concentration as well as temperature

**TABLE 1**  
Provenance and specifications of the chemicals used.

Compound	Mass fraction		Source
	Purity (%)	CAS No.	
D(–)-Ribose	0.98	50-69-1	Spectrochem. India Pvt. Ltd.
D(+)-Glucose	0.98	50-99-7	Finar Chemical Ltd., India.
Formic acid	$\geq 0.95$	64-18-6	Sigma Chemical Co.
3-Amino-1-propanol	0.99	156-87-6	Sigma Chemical Co.

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