



Cite this: *Phys. Chem. Chem. Phys.*,  
2016, **18**, 19722

## Solubility and solvation of monosaccharides in ionic liquids†

Ana Rita R. Teles,<sup>a</sup> Teresa B. V. Dinis,<sup>a</sup> Emanuel V. Capela,<sup>a</sup> Luís M. N. B. F. Santos,<sup>b</sup> Simão P. Pinho,<sup>c</sup> Mara G. Freire\*<sup>a</sup> and João A. P. Coutinho<sup>a</sup>

Herein, solubility experimental data for six monosaccharides, viz. D-(+)-glucose, D-(+)-mannose, D-(–)-fructose, D-(+)-galactose, D-(+)-xylose and L-(+)-arabinose, in four ionic liquids (ILs), at temperatures ranging from 288.2 to 348.2 K, were obtained aimed at gathering a better understanding of their solvation ability and molecular-level mechanisms which rule the dissolution process. To ascertain the chemical features that enhance the solubility of monosaccharides, ILs composed of dialkylimidazolium or tetraalkylphosphonium cations combined with the dicyanamide, dimethylphosphate or chloride anions were investigated. It was found that the ranking of the solubility of monosaccharides depends on the IL; yet, D-(+)-xylose is always the most soluble while D-(–)-fructose is the least soluble monosaccharide. The results obtained show that both the IL cation and the anion play a major role in the solubility of monosaccharides. Finally, from the determination of the respective thermodynamic properties of solution, it was found that enthalpic contributions are dominant in the solubilization process. However, the observed differences in the solubilities of monosaccharides in 1-butyl-3-methylimidazolium dicyanamide are ruled by a change in the entropy of solution.

Received 21st May 2016,  
Accepted 16th June 2016

DOI: 10.1039/c6cp03495k

www.rsc.org/pccp

## Introduction

Wood is a composite assembly of cellulose fibers connected by lignin and hemicelluloses, among other components, and is probably the renewable resource with higher potential to produce green fuels and other valuable materials.<sup>1</sup> Depending on the species, wood is composed of *circa* 35–50 wt% of cellulose, 18–30 wt% of lignin, 15–30 wt% of hemicelluloses and lower amounts of other compounds.<sup>2</sup> However, the fractionation and processing of lignocellulosic biomass is still a challenge due to its complex structure, while the current sustainable concerns require that the isolation of value-added compounds from wood has to be accomplished by environmentally-friendly and biocompatible solvents and processes.<sup>3,4</sup> Some relatively recent

approaches for biomass processing and its conversion into, or extraction of, high-value compounds are focused on the use of ionic liquids (ILs).<sup>3,5–7</sup>

ILs are defined as organic salts with melting points below 100 °C, mainly composed of large-size ions with dispersed charge. These characteristics allow ILs to display small lattice enthalpies and large entropy changes upon melting, thus favouring their liquid state at lower temperatures. Due to their ionic nature, ILs present a unique combination of physicochemical properties, such as high conductivity, negligible vapour pressure, non-flammability and a high solvation capacity to numerous polar and non-polar compounds, which is beneficial for the isolation of various biomass fractions and components.<sup>1,2,4,6,8–12</sup>

Some research groups<sup>8–13</sup> have been studying the ability of ILs to dissolve carbohydrates, including monosaccharides and disaccharides, namely glucose, mannose, xylose, sucrose and lactose, as well as high molecular weight polysaccharides, like cellulose, chitin, chitosan, inulin, pectin, starch, xylan, agarose, dextrin and cyclodextrin, aimed at identifying the most promising solvents for the fractionation of lignocellulose and the isolation of value-added compounds or materials. While for lignocellulosic biomass several ILs have demonstrated their ability to dissolve cellulose, and accordingly to pre-treat biomass,<sup>14–17</sup> currently, the conversion of biomass into smaller carbohydrates is an application of intensive demand worldwide.<sup>18</sup> As stated in the 2010 review by Zakrzewska *et al.*,<sup>13</sup> the research on the ability of ILs to dissolve oligosaccharides is still in its infancy. In particular

<sup>a</sup> CICECO – Aveiro Institute of Materials, Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal. E-mail: maragfreire@ua.pt; Fax: +351 234370084; Tel: +351 234370200

<sup>b</sup> Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, R. Campo Alegre 687, P-4169-007 Porto, Portugal

<sup>c</sup> Associate Laboratory LSRE-LCM, Departamento de Tecnologia Química e Biológica, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5301-857 Bragança, Portugal

† Electronic supplementary information (ESI) available: Water content in the studied ILs and monosaccharides, comparison data for the solubility of monosaccharides in ILs, water and methanol, as well as with literature data, and thermodynamic properties of solution of the monosaccharides in water and methanol. See DOI: 10.1039/c6cp03495k

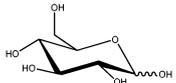
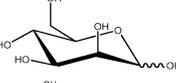
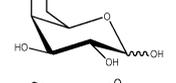
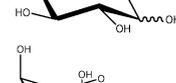
for monosaccharides, the authors<sup>13</sup> showed that the available studies have focused on the solubility of fructose and glucose in ILs based on imidazolium cations. Among these, 1-butyl-3-methylimidazolium-based ILs were revealed to be the best solvents for monosaccharides;<sup>10</sup> however, their solubility can be significantly changed by the functionalization of the alkyl side chains of the imidazolium cation, such as by the introduction of an ether group.<sup>9</sup>

In studies addressing the solubility of carbohydrates in imidazolium-based ILs, particular care was taken at high temperatures by monitoring the carbohydrate degradation and/or their "Browning effect",<sup>19–21</sup> and by determining the amount of water in the IL samples.<sup>19–23</sup> Generally, in the set of ILs studied, the solubility of saccharides at a given temperature follows the order: fructose > xylose > glucose > galactose,<sup>19,24</sup> which is closely connected to their melting properties. Albeit these recent studies contribute to an increase in the understanding on the monosaccharide solubility and their interactions with ILs, all of them reveal the need to expand that understanding, putting into evidence differences that need to be unveiled.

In addition to the experimental solubility data, other attempts for understanding the mechanisms of monosaccharide solubility in ILs can be found in the literature.<sup>25–28</sup> Youngs and co-workers<sup>28</sup> carried out molecular dynamics studies and revealed that the solvation of glucose in 1,3-dimethylimidazolium chloride results mainly from the established interactions between the chloride anion and glucose, whereas the cation only interacts weakly with the monosaccharide. Hassan *et al.*<sup>25</sup> applied *ab initio* calculations to study the impact of different ILs on the solubility of cellulose, or glucose, showing that interaction energies and hydrogen-bonding formation in systems containing glucose are higher than those with cellulose, while being governed by the hydrogen-bonding basicity and polarity of the anion. An additional interesting approach implemented by Mohan *et al.*<sup>24</sup> consisted on the screening, using COSMO-RS, of 64 ILs to dissolve monosaccharides, allowing the identification of heuristic rules to select the most adequate fluids. Furthermore, nuclear magnetic resonance (NMR),<sup>27</sup> UV-Vis and Fourier transform infrared (FTIR)<sup>26</sup> spectroscopy were used to gather a broader picture of the underlying molecular mechanisms responsible for the solvation capability of some ILs for carbohydrates. Some thermodynamic models have also been used to satisfactorily correlate the solubility data.<sup>18,23,29,30</sup>

The vast majority of studies addressing the solubility of monosaccharides in ILs were carried out using 1-alkyl-3-methylimidazolium-based fluids, and a few cases included benzotriazolium-, pyridinium-, pyrrolidinium- and ammonium-based ILs.<sup>13</sup> Therefore, it is of interest to extend the solubility studies to other classes of ILs aimed at gaining a better understanding of the IL anion and cation effects so that some structure–property relationships could be identified. Therefore, in this work, the solubilities of six monosaccharides, namely D-(+)-glucose, D-(+)-mannose, D-(–)-fructose, D-(+)-galactose, D-(+)-xylose and L-(+)-arabinose, in the temperature range from 288.2 to 348.2 K, were determined in 1-butyl-3-methylimidazolium dicyanamide, [C<sub>4</sub>C<sub>1</sub>im][N(CN)<sub>2</sub>], and 1-butyl-3-methylimidazolium

Table 1 Molecular structures of monosaccharides studied in this work

Monosaccharide	Molecular structure
D-(+)-Glucose	
D-(+)-Mannose	
D-(+)-Galactose	
D-(+)-Xylose	
L-(+)-Arabinose	
D-(–)-Fructose	

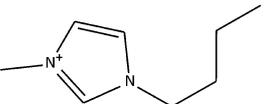
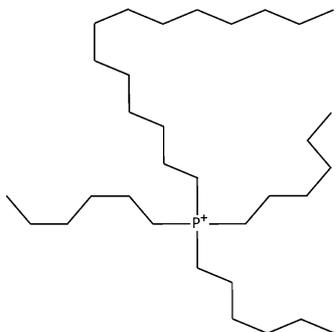
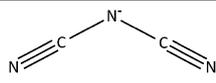
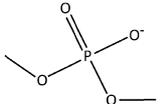
dimethylphosphate, [C<sub>4</sub>C<sub>1</sub>im][(OCH<sub>3</sub>)<sub>2</sub>PO<sub>4</sub>]. Furthermore, the solubility of glucose in the same temperature range was determined in trihexyltetradecylphosphonium dicyanamide, [P<sub>6,6,6,14</sub>][N(CN)<sub>2</sub>], and trihexyltetradecylphosphonium chloride, [P<sub>6,6,6,14</sub>]Cl. The first two ILs are more hydrophilic and completely miscible in water, while the phosphonium-based ones are more hydrophobic and form two phases in contact with water at room temperature. The chemical structures of the monosaccharides studied are presented in Table 1, while those of the ILs are shown in Table 2. The set of ILs selected allows inferring the IL cation and anion effects upon their ability to dissolve monosaccharides. On the other hand, the large set of monosaccharides investigated permits the identification of the most important features regarding their solubility in ILs. The solubility values were also compared with those reported in the literature for water<sup>31–40</sup> and methanol.<sup>32,41–44</sup> The thermodynamic functions of solution were determined and the respective solvation mechanisms are presented and discussed.

## Materials and methods

### Materials

The monosaccharides studied were D-(+)-glucose, >99.5 wt% pure from Scharlau; D-(+)-mannose, >99 wt% pure from Aldrich; D-(+)-galactose, >98.0 wt% pure from GPR Rectapur; D-(+)-xylose, 99.0 wt% pure from Carlo Erba; L-(+)-arabinose, ≥ 99.0 wt% pure from BHD Biochemicals; and D-(–)-fructose, >98.0 wt% pure from Panreac. The ILs used were 1-butyl-3-methylimidazolium dicyanamide, [C<sub>4</sub>C<sub>1</sub>im][N(CN)<sub>2</sub>], 1-butyl-3-methylimidazolium dimethylphosphate, [C<sub>4</sub>C<sub>1</sub>im][(OCH<sub>3</sub>)<sub>2</sub>PO<sub>4</sub>], trihexyltetradecylphosphonium dicyanamide, [P<sub>6,6,6,14</sub>][N(CN)<sub>2</sub>], and trihexyltetradecylphosphonium chloride, [P<sub>6,6,6,14</sub>]Cl. Imidazolium-based ILs were acquired from Iolitec, with mass fraction purities >99%,

Table 2 Chemical structures of ILs studied in this work

IL cations	
1-Butyl-3-methylimidazolium [C <sub>4</sub> C <sub>1</sub> im] <sup>+</sup>	
Trihexyltetradecylphosphonium [P <sub>6,6,6,14</sub> ] <sup>+</sup>	
IL anions	
Dicyanamide [N(CN) <sub>2</sub> ] <sup>-</sup>	
Dimethylphosphate [(OCH <sub>3</sub> ) <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	
Chloride Cl <sup>-</sup>	

and phosphonium-based ILs were kindly provided by Cytec Industries, with mass fraction purities of 97 and 93–95% for [P<sub>6,6,6,14</sub>][N(CN)<sub>2</sub>] and [P<sub>6,6,6,14</sub>]Cl, respectively. Given the low purity of phosphonium-based ILs they were further purified by repetitive washing with ultrapure water and further dried under vacuum for at least 48 h, as previously described by us.<sup>45</sup> After this process, the purity of these ILs was evaluated by <sup>31</sup>P, <sup>1</sup>H and <sup>13</sup>C NMR spectra, displaying purity mass fractions > 99%. To reduce the content of water and volatile compounds to negligible values, both ILs and monosaccharide samples were dried under high vacuum and at approximately 333 K, under continuous stirring, for a minimum of 48 h. After the drying procedure, the water content in ILs and monosaccharides was determined by Karl Fischer titration and it was found to be < 0.2 wt% for all ILs and < 0.7 wt% for all monosaccharide samples. The details of water content are presented in Table S1 in the ESI.† After the purification step, all IL and monosaccharide purities were checked by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

## Methods

**Solubility of monosaccharides in hydrophilic ILs.** Approximately 2 g of binary mixtures were prepared in closed glass vials by adding each one of the imidazolium-based ILs and each monosaccharide in excess. The mixture was left under constant stirring for at least 72 h, at constant temperature (±0.01 K), by immersing the closed glass vials in a thermostated water bath, Jubalo F12. This time period was previously optimized and although we have found

that 12 h are enough to achieve the equilibrium, 72 h were used to guarantee that in all situations the saturation was reached, particularly for the most viscous ILs and at low temperatures.

After equilibration, samples were centrifuged for 20 min at 4500 rpm, and then placed again in the water bath for 1 h, without stirring, at the desired temperature. Approximately 1 g (gravimetrically determined, ±10<sup>-5</sup> g) of each IL-saturated solution was taken and diluted in pure water in a volumetric ratio previously established and dependent on the concentration of each monosaccharide. The monosaccharide quantification was performed by a colorimetric method using dinitrosalicylic acid. 1 cm<sup>3</sup> of a standard 3,5-dinitrosalicylic acid (DNS) solution was added to 1 g of each diluted IL–monosaccharide sample, vigorously stirred, and finally placed in a water bath at 373 K for 5 min. After the reaction, samples were immersed in ice for a few minutes and further diluted in ultra-pure water up to a final volume of 10 cm<sup>3</sup>. The quantification of the reduced product 3-amino-5-nitrosalicylate was carried out by UV-Vis spectroscopy, using a SHIMADZU UV-1700, Pharma-Spec spectrometer, at a wavelength of 540 nm. Calibration curves for each monosaccharide were previously established and at least three individual vials for each set of conditions were prepared and analysed. All results regarding the monosaccharide solubility in ILs at each temperature are presented as an average value with the respective standard deviation.

## Solubility of monosaccharides in hydrophobic ILs

The equilibrium conditions and saturation of phosphonium-based ILs were achieved as described before. After reaching equilibrium, approximately 1 g (gravimetrically determined, ±10<sup>-5</sup> g) of the saturated IL–D-(+)-glucose solution was taken and 3 cm<sup>3</sup> of dichloromethane was added to induce the precipitation of the monosaccharide. The D-(+)-glucose crystals were then recovered by filtration, further washed with dichloromethane to ensure the removal of IL traces, and finally placed in an air oven at approximately 313 K and dried up to constant weight. The quantification of the monosaccharide was done by weight, within ± 10<sup>-5</sup> g. All solubility measurements were carried out at least in three independent samples. All results regarding the D-(+)-glucose solubility in ILs at each temperature are reported as an average value with the associated standard deviation.

## Results and discussion

Solubility data for monosaccharides in [C<sub>4</sub>C<sub>1</sub>im][N(CN)<sub>2</sub>] and [C<sub>4</sub>C<sub>1</sub>im][(OCH<sub>3</sub>)<sub>2</sub>PO<sub>4</sub>] are presented in Table 3 while solubility results for D-(+)-glucose in [P<sub>6,6,6,14</sub>][N(CN)<sub>2</sub>] and [P<sub>6,6,6,14</sub>]Cl are presented in Table 4. For all ILs and monosaccharides, there is an increase in the solubility with the increase in temperature.

As reported by Zakrzewska *et al.*,<sup>13</sup> the quality of experimental data available in the literature for the solubility of monosaccharides in ILs is still questionable due to the existence of large deviations between different authors. Fig. S1–S3, and Tables S2 and S3 in the ESI,† show the comparison of the solubility values of D-(+)-glucose and D-(–)-fructose in [C<sub>4</sub>C<sub>1</sub>im][N(CN)<sub>2</sub>],

**Table 3** Mole fraction solubility of monosaccharides in  $[C_4C_1im][N(CN)_2]$  and  $[C_4C_1im][(OCH_3)_2PO_4]$  at different temperatures, and the number of hydroxyl groups in each monosaccharide

Monosaccharide	<u>D-(+)-Glucose</u>	<u>D-(+)-Mannose</u>	<u>D-(+)-Galactose</u>	<u>D-(+)-Xylose</u>	<u>L-(+)-Arabinose</u>	<u>D-(−)-Fructose</u>
Number of –OH groups	5	5	5	4	4	5
T (K)	$x_{Glucose} \pm \sigma$	$x_{Mannose} \pm \sigma$	$x_{Galactose} \pm \sigma$	$x_{Xylose} \pm \sigma$	$x_{Arabinose} \pm \sigma$	$x_{Fructose} \pm \sigma$
<b><math>[C_4C_1im][N(CN)_2]</math></b>						
288.2	0.142 ± 0.007	0.172 ± 0.004	0.142 ± 0.008	0.182 ± 0.009	0.142 ± 0.009	0.132 ± 0.005
298.2	0.170 ± 0.009	0.197 ± 0.005	0.165 ± 0.007	0.208 ± 0.008	0.165 ± 0.009	0.153 ± 0.004
308.2	0.191 ± 0.006	0.226 ± 0.006	0.192 ± 0.005	0.250 ± 0.008	0.185 ± 0.008	0.178 ± 0.004
318.2	0.229 ± 0.010	0.261 ± 0.004	0.221 ± 0.009	0.280 ± 0.008	0.221 ± 0.008	0.201 ± 0.005
328.2	0.250 ± 0.007	0.301 ± 0.003	0.248 ± 0.005	0.314 ± 0.009	0.241 ± 0.007	0.220 ± 0.006
338.2	0.280 ± 0.004	0.331 ± 0.009	0.268 ± 0.009	0.355 ± 0.006	0.270 ± 0.009	0.245 ± 0.008
348.2	0.319 ± 0.005	0.390 ± 0.010	0.298 ± 0.008	0.402 ± 0.010	0.301 ± 0.009	0.275 ± 0.009
<b><math>[C_4C_1im][(OCH_3)_2PO_4]</math></b>						
288.2	0.035 ± 0.008	0.029 ± 0.007	0.070 ± 0.009	0.080 ± 0.003	0.050 ± 0.008	0.015 ± 0.003
298.2	0.045 ± 0.009	0.052 ± 0.008	0.112 ± 0.009	0.126 ± 0.005	0.078 ± 0.008	0.028 ± 0.003
308.2	0.074 ± 0.007	0.070 ± 0.009	0.182 ± 0.008	0.211 ± 0.008	0.115 ± 0.005	0.042 ± 0.003
318.2	0.132 ± 0.005	0.121 ± 0.005	0.220 ± 0.007	0.302 ± 0.009	0.182 ± 0.008	0.056 ± 0.010
328.2	0.158 ± 0.007	0.175 ± 0.008	0.344 ± 0.010	0.453 ± 0.007	0.235 ± 0.009	0.099 ± 0.005
338.2	0.232 ± 0.008	0.230 ± 0.010	0.412 ± 0.010	0.503 ± 0.009	0.332 ± 0.009	0.125 ± 0.015

**Table 4** Mole fraction solubility of D-(+)-glucose in  $[P_{6,6,6,14}][N(CN)_2]$  and  $[P_{6,6,6,14}]Cl$  at different temperatures

T (K)	<u><math>[P_{6,6,6,14}][N(CN)_2]</math></u>	<u><math>[P_{6,6,6,14}]Cl</math></u>
	$x_{Glucose} \pm \sigma$	$x_{Glucose} \pm \sigma$
288.2	0.007 ± 0.001	0.008 ± 0.001
298.2	0.009 ± 0.002	0.011 ± 0.002
308.2	0.012 ± 0.001	0.016 ± 0.002
318.2	0.013 ± 0.001	0.021 ± 0.005
328.2	0.018 ± 0.001	0.045 ± 0.005
338.2	0.027 ± 0.003	0.052 ± 0.004
348.2	0.029 ± 0.002	

and D-(+)-glucose in  $[P_{6,6,6,14}][N(CN)_2]$ , obtained by different authors. The data measured in this work show good agreement with some of the published data.<sup>21</sup> Only at higher temperatures, the D-(+)-glucose or D-(−)-fructose solubility in  $[C_4C_1im][N(CN)_2]$  shows significant differences between distinct authors. This particular fact may be assigned to the degradation of monosaccharides under these conditions, as suggested by Paduszynski *et al.*<sup>21</sup> by reporting colour changes in mixtures of glucose and  $[C_4C_1im][N(CN)_2]$  at temperatures higher than 403 K. The poor stability of monosaccharides in ILs at high temperatures was taken into consideration in this work, and for this reason, our solubility results were measured only up to 338.2 or 348.2 K, since at higher temperatures the degradation of some monosaccharides was also observed. Data measured by Carneiro *et al.*<sup>29</sup> are generally higher than the remaining available data for the solubility of D-(−)-fructose in  $[C_4C_1im][N(CN)_2]$ , while the solubility results of D-(+)-glucose in  $[P_{6,6,6,14}][N(CN)_2]$  are smaller than those measured in this work; yet, our data are in good agreement with those provided by Rosatella *et al.*<sup>11</sup> In fact, and although using different analytical techniques, the authors<sup>29</sup> also mentioned the difficulty in controlling the water content during measurements, which seems to be the main reason behind the larger deviations observed. On the other hand, the purity of ILs can also lead to different values, particularly when considering phosphonium-based ILs.

We previously described a pre-treatment method for improving their purity by consecutive washing steps with water<sup>45</sup> – an attempt also done in this work. Therefore, we believe that our phosphonium-based ILs are of higher purity which could lead to some deviations between our values and literature data.

$[C_4C_1im][N(CN)_2]$  is one of the best solvents ever reported for monosaccharides at 298 K.<sup>10,13,21,30</sup> As shown for D-(+)-glucose, a solubility value larger than that of water is observed at *circa* 298 K, as depicted in Fig. S4 in the ESI.† Similar representations for the remaining monosaccharides are shown in Fig. S5–S9 in the ESI.† Only D-(+)-mannose and D-(−)-fructose are more soluble in water than in  $[C_4C_1im][N(CN)_2]$ , at *ca.* 298 K. However, this work also shows that  $[C_4C_1im][(OCH_3)_2PO_4]$  is a better solvent than  $[C_4C_1im][N(CN)_2]$  for D-(+)-galactose and D-(+)-xylose, at higher temperatures (*cf.* Fig. S10, ESI†). A comparison of the performance of these ILs for dissolving each monosaccharide is shown in Fig. S4–S10 in the ESI.†

Although the work by Paduszynski *et al.*<sup>20</sup> demonstrated that the IL cation functionalization can improve the ability of an IL to dissolve D-(+)-glucose, the majority of studies addressing the solubility of monosaccharides in ILs are mostly focused on the effect of the IL anion.<sup>12</sup> In order to contribute to a better understanding of the IL cation effect on the solubility of monosaccharides, the solubility of D-(+)-glucose in  $[P_{6,6,6,14}]$ -based ILs, coupled with some of the best anions for dissolving monosaccharides, namely chloride and dicyanamide, was also determined in this work. D-(+)-glucose was the solute selected because it has been widely studied in ILs<sup>8–11,13,16,19–24,28,29</sup> and since it is the monomer of cellulose.<sup>12,14,16,17</sup> The solubility of D-(+)-glucose in  $[P_{6,6,6,14}]$ -based ILs is one order of magnitude lower than that observed in the imidazolium-based fluids investigated in this work (Tables 3 and 4). Therefore, all results gathered in this work clearly reveal that both the IL anion and the cation play a significant role in the monosaccharide solubility.

Fig. 1 and 2 depict the solubility of all monosaccharides, expressed as the natural logarithm of the mole fraction,  $\ln x_{Monosaccharide}$ , as a function of the reciprocal temperature,

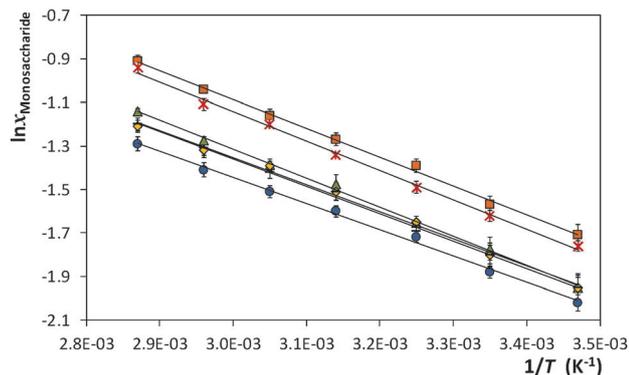


Fig. 1 Solubility of monosaccharides, as the natural logarithm of the mole fraction,  $\ln x_{\text{Monosaccharide}}$ , in  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ , versus the reciprocal temperature ( $1/T$ ): ■, D-(+)-xylose; ×, D-(+)-mannose; ▲, D-(+)-glucose; ◆, D-(+)-galactose; —, L-(+)-arabinose; and ●, D-(-)-fructose.

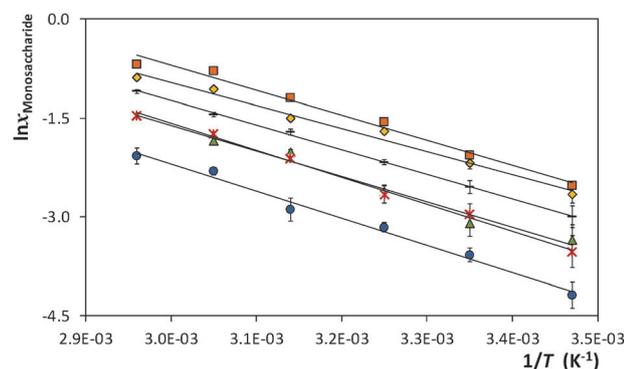


Fig. 2 Solubility of monosaccharides, as the natural logarithm of the mole fraction,  $\ln x_{\text{Monosaccharide}}$ , in  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_4]$ , versus the reciprocal temperature ( $1/T$ ): ■, D-(+)-xylose; ◆, D-(+)-galactose; —, L-(+)-arabinose; ▲, D-(+)-glucose; ×, D-(+)-mannose; and ●, D-(-)-fructose.

$1/T$ , in  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$  and in  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_4]$ , respectively. The corresponding equations are given in the ESI,† Table S4. At a given temperature, the solubility of monosaccharides in  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$  decreases according to the order: D-(+)-xylose > D-(+)-mannose > D-(+)-glucose  $\approx$  D-(+)-galactose  $\approx$  L-(+)-arabinose > D-(-)-fructose (Fig. 1), whereas the solubility in  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_4]$  decreases in the following sequence: D-(+)-xylose > D-(+)-galactose > L-(+)-arabinose > D-(+)-mannose  $\approx$  D-(+)-glucose > D-(-)-fructose (Fig. 2). While D-(+)-xylose and D-(-)-fructose are, respectively, the most and less soluble saccharide in both ILs, differences between the two sequences, most notably for D-(+)-galactose and D-(+)-mannose, are not simple to explain. It is also of particular interest to remark that in recent works,<sup>19,24</sup> D-(-)-fructose was shown to be often the most soluble monosaccharide in imidazolium-based ILs, while in this work it is the less soluble monosaccharide.

In order to compare and interpret the solvation mechanisms of monosaccharides in ILs, the enthalpy of solution,  $\Delta H_{\text{sol}}$ , the Gibbs free energy of solution,  $\Delta G_{\text{sol}}$ , and the entropy of solution,  $\Delta S_{\text{sol}}$ , were determined at 298 K using the following equations:<sup>46</sup>

$$\Delta G_{\text{sol}} = -RT \ln x_{\text{Monosaccharide}} \quad (1)$$

$$\frac{\Delta H_{\text{sol}}}{RT^2} = \left( \frac{\partial \ln x_{\text{Monosaccharide}}}{\partial T} \right)_p \quad (2)$$

$$\Delta S_{\text{sol}} = R \left( \frac{\partial T \ln x_{\text{Monosaccharide}}}{\partial T} \right)_p \quad (3)$$

where  $x_{\text{Monosaccharide}}$  is the mole fraction solubility of each monosaccharide in the IL,  $R$  is the ideal gas constant,  $T$  is the absolute temperature, and the subscript  $p$  indicates isobaric conditions.

All solution properties are presented in Table 5. The obtained van't Hoff<sup>47</sup> plots are all linear (with  $R^2$  values ranging between 0.98 and 1.00, except for D-(+)-glucose in  $[\text{P}_{6,6,6,14}]\text{Cl}$  with a  $R^2$  value of 0.97). This good linearity is an indication of a negligible heat capacity change in the temperature range addressed in this work. The melting properties, namely the enthalpy of melting,  $\Delta H_{\text{m}}$ , and the temperature of melting,  $T_{\text{m}}$ , of all monosaccharides are also reported in Table 5, since they are helpful to rationalize the solubility data and mechanisms of solvation discussed below.

The solubilisation of all studied monosaccharides in ILs is an endothermic process that is reflected by their solubility increase with temperature. Within the experimental uncertainty of the data, in both  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$  and  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_4]$ , the enthalpies of solution are poorly dependent on the monosaccharide nature, with values of  $\approx 11$  and  $\approx 32$   $\text{kJ mol}^{-1}$  for  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$  and  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_4]$ , respectively.

Fig. 3 depicts a schematic representation of the several steps involved, aimed at gaining a better understanding of the solubility and solvation processes of monosaccharides in ILs. The solution/solvation process is divided into two main steps: Step 1, comprising cohesive interactions of monosaccharides, and Step 2, comprising interactions between monosaccharides and ILs as well as the IL cavitation. The cavitation energy (in Step 2) is defined as the work required for the formation of a surface at the solvent to accommodate a given solute, and is entropically and enthalpically unfavourable.<sup>48</sup> The similarity between the enthalpies of solution observed within different monosaccharides in the same IL suggests that the enthalpy of disruption of hydrogen-bonds and van der Waals interactions in the solid monosaccharides (in Step 1) is partially compensated by the formation of new hydrogen-bonds between these and ILs (in Step 2). This similarity is not observed for other solvents, as shown in the values reported in Table S5 in the ESI,† where the enthalpies of solution in water and methanol are highly distinct for the different monosaccharides, and where a higher dispersion in the entropy of solution is also observed. If data available for the solubility of some monosaccharides cannot guarantee very precise estimations, it is important to remark that enthalpies of solution in water measured by solution calorimetry<sup>49</sup> are in acceptable agreement with the values shown in Table S5 in the ESI.†

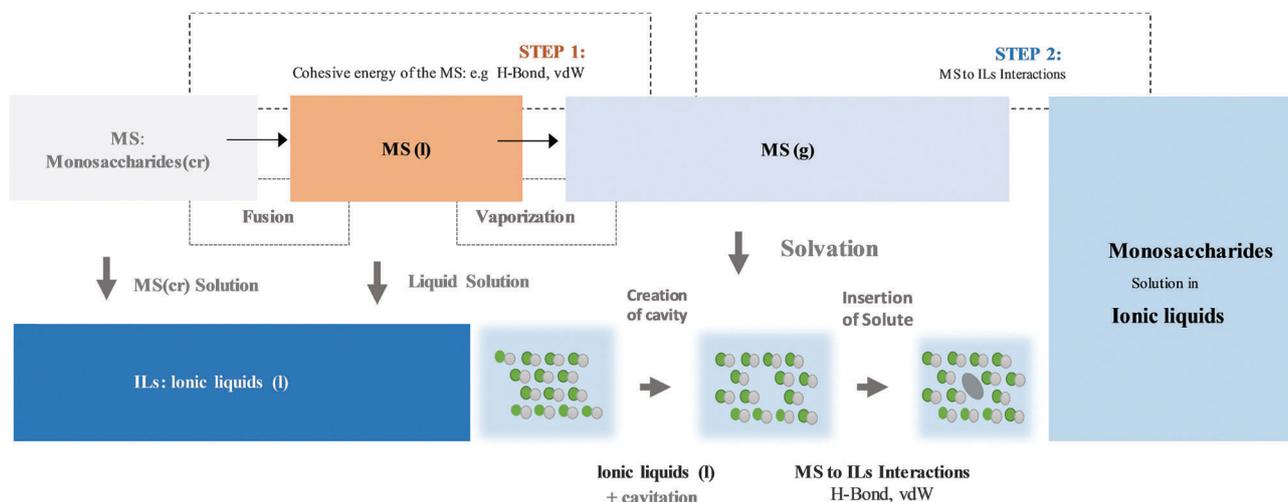
The mole fraction solubility of monosaccharides in  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ , at approximately 298 K, is close to 0.2 (1:4) for D-(+)-xylose and D-(+)-mannose, and to 0.17 (1:5) for the remaining carbohydrates, indicating that each monosaccharide is solvated by

**Table 5** Melting temperature,  $T_m$  (in K), and thermodynamic solution properties (in  $\text{kJ mol}^{-1}$ ) of monosaccharides in ILs at 298 K: enthalpy of solution,  $\Delta H_{\text{sol}}$ , entropy of solution,  $T\Delta S_{\text{sol}}$ , Gibbs free energy of solution,  $\Delta G_{\text{sol}}$ , and the respective uncertainties (within brackets)

Monosaccharide	$\Delta H_m$	$T_m$	$[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$			$[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_4]$		
			$\Delta H_{\text{sol}}$	$T\Delta S_{\text{sol}}$	$\Delta G_{\text{sol}}$	$\Delta H_{\text{sol}}$	$T\Delta S_{\text{sol}}$	$\Delta G_{\text{sol}}$
D-(+)-Glucose	32.3 <sup>50</sup>	423.2 <sup>51</sup>	11.04 (0.77)	6.65 (0.86)	4.39 (0.09)	31.98 (5.70)	24.30 (6.25)	7.68 (0.55)
D-(+)-Mannose	24.7 <sup>50</sup>	407.2 <sup>50</sup>	11.26 (0.78)	7.24 (0.83)	4.02 (0.05)	33.76 (3.80)	26.43 (4.75)	7.33 (0.95)
D-(−)-Fructose	26.0 <sup>52</sup>	378.2 <sup>53</sup>	10.03 (0.54)	5.37 (0.62)	4.66 (0.08)	34.08 (4.71)	25.22 (4.98)	8.86 (0.27)
D-(+)-Galactose	43.8 <sup>50</sup>	436.2 <sup>50</sup>	10.33 (0.73)	5.87 (0.85)	4.46 (0.12)	28.88 (4.49)	23.46 (4.71)	5.42 (0.22)
D-(+)-Xylose	31.7 <sup>50</sup>	423.2 <sup>51</sup>	10.97 (0.57)	7.08 (0.68)	3.89 (0.10)	31.18 (5.36)	26.05 (5.95)	5.13 (0.59)
L-(+)-Arabinose	35.8 <sup>50</sup>	428.7 <sup>52</sup>	10.47 (0.66)	6.01 (0.80)	4.46 (0.14)	30.71 (2.13)	24.38 (2.04)	6.33 (0.64)

Monosaccharide	$\Delta H_m$	$T_m$	$[\text{P}_{6,6,6,14}][\text{N}(\text{CN})_2]$			$[\text{P}_{6,6,6,14}]\text{Cl}$		
			$\Delta H_{\text{sol}}$	$T\Delta S_{\text{sol}}$	$\Delta G_{\text{sol}}$	$\Delta H_{\text{sol}}$	$T\Delta S_{\text{sol}}$	$\Delta G_{\text{sol}}$
D-(+)-Glucose	32.3 <sup>50</sup>	423.2 <sup>51</sup>	20.24 (3.30)	8.64 (3.71)	11.60 (0.41)	33.12 (7.71)	21.81 (8.18)	11.31 (0.47)



**Fig. 3** Schematic representation of various steps involved in the solubility/solvation process of monosaccharides in ILs.

four or five IL ion pairs under the saturation conditions (a list of the number of  $-\text{OH}$  groups in monosaccharides is presented in Table 3). Since the enthalpies of sublimation associated with Step 1, judging by the value<sup>54</sup> of  $160 \text{ kJ mol}^{-1}$  for carbohydrate alcohols, are far more important than the enthalpies of melting, of about  $25 \text{ kJ mol}^{-1}$  per hydrogen-bond, it means that the solvation of each monosaccharide in the IL is accomplished by the formation of hydrogen-bonding and dispersive-type interactions, which correspond to the enthalpies associated with Step 2. This view is consistent with a low and positive enthalpy of solution due to the formation of hydrogen-bonds, and a low solution entropy which indicates a specific interaction. Even if the solubility process is controlled by enthalpic contributions, the differences in the solubility magnitude between monosaccharides are difficult to interpret as the difference between the solution entropies and enthalpies is small, both following approximately the same trend. The cavitation energy (in Step 2) is expected to be very similar for various monosaccharides in the same IL, but it changes with the IL. For instance, the significantly lower solubility of D-(+)-glucose in  $[\text{P}_{6,6,6,14}][\text{N}(\text{CN})_2]$  than in  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$  is enthalpically driven and could be partially

associated with a higher cavitation energy displayed by the large-size  $[\text{P}_{6,6,6,14}][\text{N}(\text{CN})_2]$ .

The solubility of monosaccharides in a given IL is not directly related to their melting properties, but dominated by the non-ideality of the solution, where the interplay between the higher cohesive energy of monosaccharides and their strong interactions (dispersive and hydrogen-bonding) with ILs reflect the solvation of the hydroxyl groups. Nevertheless, the solubility of monosaccharides in ILs does not strictly follow the number of  $-\text{OH}$  groups in each monosaccharide and does not significantly increase with the number of hydroxyl groups in equatorial position, contrary to that observed for the solvation of monosaccharides in water.<sup>49</sup>

For  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_4]$ , the estimated properties of solution, presented in Table 5, are closer to those displayed in methanol (*cf.* Table S5, ESI†). With this IL, the enthalpies of solution are closer to the enthalpies of melting, but they display a well-defined decrease with the increase on the enthalpy of melting. Actually, two monosaccharides, namely D-(+)-mannose and D-(−)-fructose, present enthalpies of solution higher than their enthalpies of melting, while those displayed by L-(+)-arabinose and D-(+)-galactose are comparatively lower. Nonetheless, for the remaining

monosaccharides, the enthalpies of solution are, within the experimental uncertainty, identical to their enthalpies of melting. While for D-(+)-mannose and D-(-)-fructose the activity coefficients are generally higher than 1, revealing thus unfavourable IL–monosaccharide interactions, for the remaining monosaccharides, low activity coefficients are present, revealing therefore strong and favourable interactions (although they are significantly affected by temperature). Whereas for D-(+)-xylose and D-(+)-glucose the similarities observed between  $\Delta H_{\text{sol}}$  and  $\Delta H_{\text{m}}$  follow the activity coefficient values, for D-(+)-galactose and D-(+)-arabinose the differences observed between these enthalpic parameters ( $\Delta H_{\text{sol}}$  lower than  $\Delta H_{\text{m}}$ ) are reflected by an increase of their activity coefficient values with temperature.

The mole fraction solubility of monosaccharides in  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_4]$ , at ca. 298 K, is lower than in  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ . The solvation of one monosaccharide molecule in  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_4]$  requires 8 to 35 IL ion pairs, which indicates that the solvation, unlike previously observed with  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ , is not related to the number of available hydroxyl groups in the monosaccharide. This is further confirmed by the solution properties – the enthalpy of solution is much higher in  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_4]$  than in  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$  – revealing the existence of unfavourable interactions. The surface tension of  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_4]$  is 11 mN m<sup>-1</sup> at 298 K, which is lower than that of  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ . This fact is an indication of a relatively lower cavitation energy (formation of a surface in the solvent) in the  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_4]$  IL.<sup>56</sup> Although the solvation of monosaccharides in  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$  is, as discussed above, highly dependent on the number and strength of established hydrogen-bonds between the IL anion and the hydroxyl groups of the monosaccharide, the solvation of monosaccharides in  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_2]$  is reflected by a different nature and it is highly connected to the enthalpy of solution. Consequently, for higher temperatures,  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_2]$  becomes a better solvent to dissolve some monosaccharides than  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ .

The higher entropic contribution ( $T\Delta S_{\text{sol}}$ ) in the solubility of monosaccharides in  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_4]$  and in  $[\text{P}_{6,6,6,14}\text{Cl}]$ , ( $\approx 20$  to  $26$  kJ mol<sup>-1</sup>), when compared with  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$  and  $[\text{P}_{6,6,6,14}][\text{N}(\text{CN})_2]$  ( $\approx 5$  to  $9$  kJ mol<sup>-1</sup>), is related to the low directional interaction potential of the  $[(\text{OCH}_3)_2\text{PO}_4]^-$  and  $\text{Cl}^-$  anions. The high entropy of solution of monosaccharides in  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_4]$  (driven by the high solubility) can be explained by the high number of oxygen atoms in this IL anion, and therefore to its potential to hydrogen-bond with hydroxyl groups of monosaccharides in multiple arrangements.

In addition to the effect of the IL anion, a relevant effect of the IL cation was found in this work – there is a decrease of one order of magnitude in the mole fraction solubility of glucose from  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$  to  $[\text{P}_{6,6,6,14}][\text{N}(\text{CN})_2]$  (Fig. 4). The corresponding equations of the linear functions shown in Fig. 4 are given in ESI,† Table S4. The estimated enthalpy of solution for dicyanamide-based ILs is about two times larger in the phosphonium – than in the imidazolium-based compound. On the other hand, the entropy of solution is slightly higher in  $[\text{P}_{6,6,6,14}][\text{N}(\text{CN})_2]$ , suggesting that the observed significantly lower solubility of D-(+)-glucose in  $[\text{P}_{6,6,6,14}][\text{N}(\text{CN})_2]$  is enthalpically driven. Moreover, a

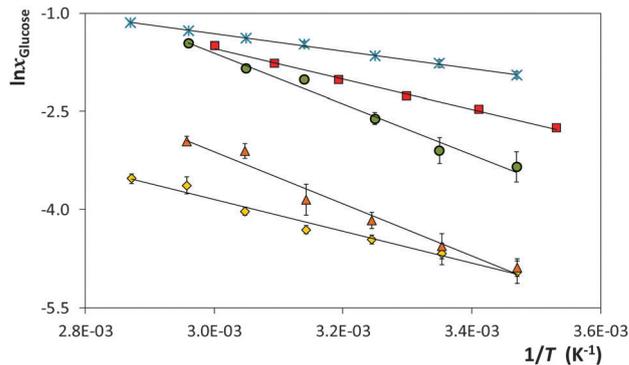


Fig. 4 Solubility of D-(+)-glucose, as the natural logarithm of the mole fraction,  $\ln X_{\text{Glucose}}$ , in the studied ILs and water, versus the reciprocal temperature ( $1/T$ ):  $\times$ ,  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ ;  $\blacksquare$ , water;<sup>51</sup>  $\bullet$ ,  $[\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_2]$ ;  $\blacktriangle$ ,  $[\text{P}_{6,6,6,14}\text{Cl}]$ ; and  $\blacklozenge$ ,  $[\text{P}_{6,6,6,14}][\text{N}(\text{CN})_2]$ .

decrease in the intensity of hydrogen-bond interactions between phosphonium-based ILs and monosaccharides due to the higher cavitation energy associated with the bulky phosphonium cation is expected. The higher solution properties of D-(+)-glucose in  $[\text{P}_{6,6,6,14}\text{Cl}]$  also reflect a decrease in the number and intensity of hydrogen-bonding-type interactions between this IL and monosaccharides. In summary, the set of results for  $[\text{P}_{6,6,6,14}\text{Cl}]$  and  $[\text{P}_{6,6,6,14}][\text{N}(\text{CN})_2]$  corroborates the high relevance of the IL cation to the solubility of monosaccharides, whereas the decrease in the monosaccharide solubility in trihexyltetradecylphosphonium-based ILs is mainly related to their bulky size when compared with imidazolium-based counterparts.

## Conclusions

Aimed at gaining a better understanding of the enhanced solubility of monosaccharides in ILs, in this work, the solubility of six monosaccharides was determined in four ILs in a broad temperature range. At 298 K, the solubility of D-(+)-glucose decreases in the following order:  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2] > [\text{C}_4\text{C}_1\text{im}][(\text{OCH}_3)_2\text{PO}_2] > [\text{P}_{6,6,6,14}][\text{N}(\text{CN})_2] > [\text{P}_{6,6,6,14}\text{Cl}]$ .

The solution properties were additionally determined in order to rationalize the monosaccharide solubilisation phenomenon in ILs. Generally, enthalpic contributions were found to be dominant and independent of the monosaccharide. However, the entropic contributions cannot be discarded since they support the differences observed in the solubility of monosaccharides in  $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ . The effect of the IL cation is highly relevant and it was found to be enthalpically driven. This fact can be explained by the higher cavitation energy of  $[\text{P}_{6,6,6,14}][\text{N}(\text{CN})_2]$  and by the decrease in the intensity of IL–monosaccharide hydrogen-bonding interactions.

## Acknowledgements

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), the project CIQUP Centro

de Investigação em Química da Universidade do Porto (PEst-C/UI0081/2013) and the LSRE-LCM Associate Laboratory (POCI-01-0145-FEDER-006984), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. This research received funding from the European Research Council under the European Union's Seventh Framework Programme (FP7/2007–2013)/ERC grant agreement no. 337753.

## Notes and references

- M. N. Belgacem and A. Gandini, in *Monomers, Polymers and Composites from Renewable Resources*, ed. M. N. Belgacem and A. Gandini, Elsevier, Amsterdam, 1st edn, 2008, ch. 20, pp. 419–431.
- E. Sjöström, *Wood chemistry: Fundamentals and applications*, Academic Press (an imprint of Elsevier), New York, 1993.
- P. Maki-Arvela, I. Anugwom, P. Virtanen, R. Sjöholm and J. P. Mikkola, *Ind. Crops Prod.*, 2010, **32**, 175–201.
- D. A. Fort, R. C. Remsing, R. P. Swatloski, P. Moyna, G. Moyna and R. D. Rogers, *Green Chem.*, 2007, **9**, 63–69.
- M. FitzPatrick, P. Champagne, M. F. Cunningham and R. A. Whitney, *Bioresour. Technol.*, 2010, **101**, 8915–8922.
- S. Murugesan and R. J. Linhardt, *Curr. Org. Synth.*, 2005, **2**, 437–451.
- S. Zhu, *J. Chem. Technol. Biotechnol.*, 2008, **83**, 777–779.
- S. A. Forsyth, D. R. MacFarlane, R. J. Thomson and M. von Itzstein, *Rapid, clean, and mild O-acetylation of alcohols and carbohydrates in an ionic liquid*, 7th edn, 2002.
- N. Kimizuka and T. Nakashima, *Langmuir*, 2001, **17**, 6759–6761.
- Q. B. Liu, M. H. A. Janssen, F. van Rantwijk and R. A. Sheldon, *Green Chem.*, 2005, **7**, 39–42.
- A. A. Rosatella, L. C. Branco and C. A. M. Afonso, *Green Chem.*, 2009, **11**, 1406–1413.
- R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, 2002, **124**, 4974–4975.
- M. E. Zakrzewska, E. Bogel-Lukasik and R. Bogel-Lukasik, *Energy Fuels*, 2010, **24**, 737–745.
- A. Pinkert, K. N. Marsh and S. Pang, *Ind. Eng. Chem. Res.*, 2010, **49**, 11121–11130.
- M. G. Freire, A. R. R. Teles, M. A. A. Rocha, B. Schröder, C. M. S. S. Neves, P. J. Carvalho, D. V. Evtuguin, L. M. N. B. F. Santos and J. A. P. Coutinho, *J. Chem. Eng. Data*, 2011, **56**, 4813–4822.
- B. Medronho, A. Romano, M. G. Miguel, L. Stigsson and B. Lindman, *Cellulose*, 2012, **19**, 581–587.
- S. Zhang, J. Sun, X. Zhang, J. Xin, Q. Miao and J. Wang, *Chem. Soc. Rev.*, 2014, **43**, 7838–7869.
- E.-S. R. E. Hassan, F. Mutelet, S. Pontvianne and J.-C. Moise, *Environ. Sci. Technol.*, 2013, **47**, 2809–2816.
- C. Carrero-Carralero, L. Ruiz-Aceituno, L. Ramos, F. Javier Moreno and M. Luz Sanz, *Ind. Eng. Chem. Res.*, 2014, **53**, 13843–13850.
- K. Padaszynski, M. Okuniewski and U. Domanska, *J. Chem. Thermodyn.*, 2016, **92**, 81–90.
- K. Padaszynski, M. Okuniewski and U. Domanska, *Ind. Eng. Chem. Res.*, 2013, **52**, 18482–18491.
- L. J. A. Conceição, E. Bogel-Lukasik and R. Bogel-Lukasik, *RSC Adv.*, 2012, **2**, 1846–1855.
- A. P. Carneiro, O. Rodriguez and E. A. Macedo, *Fluid Phase Equilib.*, 2012, **314**, 22–28.
- M. Mohan, V. V. Goud and T. Banerjee, *Fluid Phase Equilib.*, 2015, **395**, 33–43.
- E.-S. R. E. Hassan, F. Mutelet and M. Bouroukba, *Carbohydr. Polym.*, 2015, **127**, 316–324.
- J. Kiefer, K. Obert, A. Bösmann, T. Seeger, P. Wasserscheid and A. Leipertz, *ChemPhysChem*, 2008, **9**, 1317–1322.
- R. C. Remsing, G. Hernandez, R. P. Swatloski, W. W. Masefski, R. D. Rogers and G. Moyna, *J. Phys. Chem. B*, 2008, **112**, 11071–11078.
- T. G. A. Youngs, C. Hardacre and J. D. Holbrey, *J. Phys. Chem. B*, 2007, **111**, 13765–13774.
- A. P. Carneiro, O. Rodriguez and E. A. Macedo, *Ind. Eng. Chem. Res.*, 2013, **52**, 3424–3435.
- A. P. Carneiro, C. Held, O. Rodriguez, G. Sadowski and E. A. Macedo, *J. Phys. Chem. B*, 2013, **117**, 9980–9995.
- L. A. Alves, J. B. Almeida e Silva and M. Giuliatti, *J. Chem. Eng. Data*, 2007, **52**, 2166–2170.
- A. M. Peres and E. A. Macedo, *Ind. Eng. Chem. Res.*, 1997, **36**, 2816–2820.
- T. Alavi, G. Pazuki and A. Raisi, *J. Food Sci.*, 2014, **79**, E839–E848.
- C. E. Crestani, A. Bernardo, C. B. B. Costa and M. Giuliatti, *J. Chem. Eng. Data*, 2013, **58**, 3039–3045.
- R. N. Goldberg, B. E. Lang, B. Coxon and S. R. Decker, *J. Chem. Thermodyn.*, 2012, **52**, 2–10.
- M. C. Gray, A. O. Converse and C. E. Wyman, *Appl. Biochem. Biotechnol.*, 2003, **105**, 179–193.
- R. F. Jackson, C. G. Silsbee and M. J. Proffitt, *Sci. Pap. Bur. Stand.*, 1926, **519**, 587–617.
- L. Jiang, S. Li, J. Jiang, J. Qiu and P. Wang, *J. Mol. Liq.*, 2015, **211**, 406–410.
- S. O. Jónsdóttir, S. A. Cooke and E. A. Macedo, *Carbohydr. Res.*, 2002, **337**, 1563–1571.
- E. A. Martínez, M. Giuliatti, M. Uematsu, S. Derenzo and J. B. Almeida e Silva, *Chem. Prod. Process Model.*, 2011, **6**, 1934–2659.
- E. A. Macedo and A. M. Peres, *Ind. Eng. Chem. Res.*, 2001, **40**, 4633–4640.
- F. Montañés, A. Olano, E. Ibáñez and T. Fornari, *AIChE J.*, 2007, **53**, 2411–2418.
- H. Stephen and T. Stephen, *Solubilities of Inorganic and Organic Compounds: Binary Systems*, Pergamon Press, Oxford, 1963.
- R.-J. van Putten, J. G. M. Winkelman, F. Keihan, J. C. van der Waal, E. de Jong and H. J. Heeres, *Ind. Eng. Chem. Res.*, 2014, **53**, 8285–8290.
- C. M. S. S. Neves, J. F. O. Granjo, M. G. Freire, A. Robertson, N. M. C. Oliveira and J. A. P. Coutinho, *Green Chem.*, 2011, **13**, 1517–1526.
- M. A. R. Martins, C. M. S. S. Neves, K. A. Kurnia, A. Luis, L. M. N. B. F. Santos, M. G. Freire, S. P. Pinho

- and J. A. P. Coutinho, *Fluid Phase Equilib.*, 2014, **375**, 161–167.
- 47 A. J. Queimada, F. L. Mota, S. P. Pinho and E. A. Macedo, *J. Phys. Chem. B*, 2009, **113**, 3469–3476.
- 48 A. Ben-Naim, *Molecular Theory of Solutions*, Oxford University Press, 1st edn, 2006.
- 49 R. V. Jasra and J. C. Ahluwalia, *J. Solution Chem.*, 1982, **11**, 325–338.
- 50 Y. H. Roos, *Carbohydr. Res.*, 1993, **238**, 39–48.
- 51 A. Raemy and T. F. Schweizer, *J. Therm. Anal.*, 1983, **28**, 95–108.
- 52 J. A. Dean and N. A. Lange, *Lange's handbook of chemistry*, McGraw-Hill Book Company, New York, 13th edn, 1985.
- 53 O. Ferreira, E. A. Brignole and E. A. Macedo, *Ind. Eng. Chem. Res.*, 2003, **42**, 6212–6222.
- 54 G. Barone, G. Dellagatta, D. Ferro and V. Piacente, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 75–79.
- 55 N.-n. Ren, Y.-h. Gong, Y.-z. Lu, H. Meng and C.-x. Li, *J. Chem. Eng. Data*, 2014, **59**, 189–196.
- 56 L. G. Sánchez, J. R. Espel, F. Onink, G. W. Meindersma and A. B. de Haan, *J. Chem. Eng. Data*, 2009, **54**, 2803–2812.