

# Solubility of bio-sourced feedstocks in 'green' solvents†

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Received 11th June 2010, Accepted 28th July 2010

DOI: 10.1039/c0gc00205d

A group of 14 different bio-sourced, renewable feedstocks (homoserine, **1**; glutamic acid, **2**; aspartic acid, **3**; 2,5-furandicarboxylic acid, **4**; fumaric acid, **5**; oxalacetic acid, **6**; tartaric acid, **7**; malic acid, **8**; succinic acid, **9**; levulinic acid, **10**;  $\gamma$ -hydroxybutyrolactone, **11**; xylitol, **12**; mannitol, **13**; sorbitol, **14**) have been examined for their solubility/miscibility in a variety of 'green' solvents, including water, supercritical carbon dioxide (scCO<sub>2</sub>), and ionic liquids. Two other bio-based compounds 5-hydroxymethylfurfural, **15**, and D-xylose, **16**, were studied in selected solvents. Trends in solubility have been assessed so that these data may be extrapolated to help predict solubilities of other related compounds. For example, **10**, **11** and **15** all demonstrated appreciable solubility in scCO<sub>2</sub>, as they possess weak intermolecular interactions. The dicarboxylic acids studied (**4**–**9**) all proved soluble in modified scCO<sub>2</sub> (by use of MeOH as a cosolvent). While the polyols (**12**–**14**) and **1** were insoluble in scCO<sub>2</sub> but water of various pHs and ionic liquids proved adept at their dissolution. Some of the amino acids studied (**2** and **3**) were only soluble in water with an adjustment of pH.

## Introduction

Many modern synthetic organic chemicals and materials are made from non-renewable feedstocks. Given today's environmental concerns, the search for sustainable feedstocks capable of conversion into these chemicals is of increasing importance.<sup>1,2</sup> Industrially, several companies are already using bio-sourced compounds in the preparation of polymers. As outlined by Bozell and Petersen,<sup>2</sup> a range of renewable starting materials (polysaccharides, simple sugars, furan-derivatives, acids and alcohols) are being studied by researchers worldwide, including (but not limited to) inulins, cellulose, glucose, fructose, and glycerol.<sup>3</sup> These endeavours have demonstrated the viability of such reagents as new sources of valuable chemicals and precursors, such as: 1,3-propanediol, used in polyester manufacturing;<sup>4</sup>  $\gamma$ -butyrolactone, which can act as a THF precursor;<sup>5</sup> 1,3-dihydroxyacetone, a major component of sunless tanning products;<sup>6</sup> furfural, 5-hydroxymethylfurfural and 5-(chloromethyl)furfural, versatile chemical intermediates and biofuel precursors.<sup>7–9</sup>

While the source of reagents is of course important, in terms of sustainability, the way in which the reaction is carried out is another important consideration. As such, investigations into solvent replacement have blossomed in recent years. Obviously, the greenest solvent is no added solvent at all.<sup>10</sup> Recently, 'solvent free' conversions of renewable feedstocks have been reported including microwave-assisted conversion of glucose to

lactic acid using alumina-supported KOH.<sup>11</sup> However, even with modern understanding of such systems, various limitations (e.g. insufficient heat and mass transfer) prevent the use of 'solvent free' conditions in many situations. It is in these situations where alternative solvents play an important role.

Volatile organic compounds (VOCs) such as benzene, dichloromethane, chloroform, and pyridine, once extensively used, are being phased out worldwide as a result of their hazardous nature.<sup>12</sup> They present a variety of environmental and health concerns, including toxicity, carcinogenicity, flammability and environmental persistence/contamination.<sup>10</sup> These concerns have led to an upsurge of research into alternative solvents and their applicability. One type of 'green' solvent is actually a subcategory of VOCs. Renewable, bio-sourced organic compounds may still possess some undesirable qualities, such as flammability, but are otherwise superior to traditional VOCs in their biodegradability and low toxicity.<sup>10</sup>

Other alternative solvents that have been extensively studied during the last two decades include water, supercritical carbon dioxide (scCO<sub>2</sub>), and ionic liquids, all of which will be discussed in this work. Combining the use of such alternative solvents<sup>13</sup> with renewable, bio-sourced reagents would make for a much greener process overall. As such, an understanding of the solubility of 'green' feedstocks in a variety of different solvents would be advantageous.

## Results and discussion

The 14 compounds illustrated in Fig. 1 are all available from biomass. Many even have the distinction of being identified by the US Department of Energy as being 'Platform' chemicals.<sup>14</sup> They are grouped within Fig. 1 according to functional groups: **1**–**3** are amino acids, **4**–**9** are dicarboxylic acids, **10** and **11** are liquids and are an acid and ester, respectively, whereas **12**–**14** are polyols. Herein, we describe the solubility of these compounds

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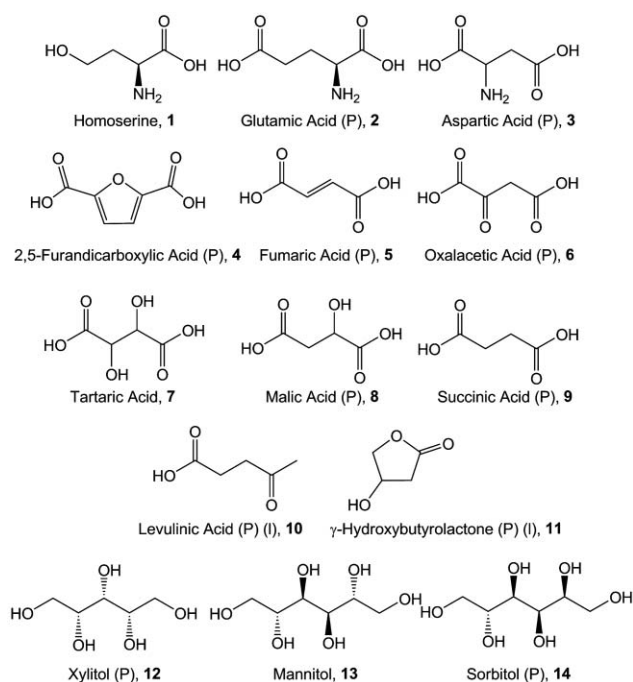
† Electronic supplementary information (ESI) available: Example video of phase change (precipitation) for **4** in MeOH-modified scCO<sub>2</sub> at 45 °C. Cloud point data was obtained with slower adjustment of pressure compared with this video. See DOI: 10.1039/c0gc00205d

**Table 1** Solubility data for bio-sourced molecules in aqueous solution, alcohols, chloroform and diethyl ether<sup>a</sup>

Compound	pK <sub>a</sub> <sup>b</sup>	LogP <sub>oct/wat</sub> <sup>b</sup>	Solvents						
			Water, pH 7	Water, pH 4.7	Water, pH 9.6	Methanol	Ethanol	Chloroform	Diethyl ether
<b>1<sup>d</sup></b>	2.19, 9.21	-2.785 <sup>c</sup>	<1 min	<1 min	<1 min	—	—	—	—
<b>2</b>	2.13, 4.31, 9.58	-3.386	—	—	<1 min	—	—	—	—
<b>3</b>	1.99, 3.90, 9.90	-3.236	—	24 h	<1 min	—	—	—	—
<b>4<sup>d</sup></b>	2.60, 3.55	-0.913 <sup>c</sup>	—	2 min	2 min	24 h	—	—	—
<b>5</b>	3.03, 4.44	-0.748	—	2 min	3 min	24 h	24 h	—	—
<b>6</b>	2.22, 3.89, 13.03 <sup>e</sup>	-1.600 <sup>c</sup>	<1 min	<1 min	<1 min	<1 min	<1 min	—	—
<b>7</b>	2.98, 4.34	-2.459 <sup>c</sup>	<1 min	—	<1 min	1 min	1 min	—	—
<b>8</b>	3.40, 5.11	-1.984	<1 min	<1 min	<1 min	<1 min	1 min	—	—
<b>9</b>	4.16, 5.61	-0.590	1 min	<1 min	<1 min	<1 min	1 min	—	—
<b>10</b>	4.62	-0.490 <sup>c</sup>	Miscible	Miscible	Miscible	Miscible	Miscible	Miscible	Miscible
<b>11</b>	12.87	-1.901 <sup>c</sup>	Miscible	Miscible	Miscible	Miscible	Miscible	Miscible	Miscible
<b>12</b>	13.70	-2.068 <sup>c</sup>	<1 min	<1 min	<1 min	—	—	—	—
<b>13</b>	13.50	-3.100	<1 min	<1 min	<1 min	—	—	—	—
<b>14</b>	13.00	-2.912 <sup>c</sup>	<1 min	<1 min	<1 min	—	—	—	—

<sup>a</sup> Time required (at room temperature) to dissolve 100 mg of compound in 5.00 mL of each respective solvent. This corresponds to a concentration of 20 mg mL<sup>-1</sup>. Experiments were performed by simply combining the solute and solvent in a 20 mL scintillation vial, swirling, observing for ten minutes and then leaving the sample capped overnight at room temperature. Entries marked as '—' were not soluble after a 24 h period.

<sup>b</sup> Physical constants obtained from *CRC handbook of chemistry and physics*, 84th edition, CRC Press, Boca Raton, Florida, 2003, and *Data for biochemical research*, 3rd edition, Oxford University Press, New York, New York, 1986. <sup>c</sup> Predicted octanol-water partition coefficient from <http://pirika.com/chem/TCPEE/LOGKOW/ourlogKow.htm> or ACD/LogP freeware. <sup>d</sup> 20 mg of compound and 2 mL of solvent were used for studies of homoserine, **1** and 2,5-furandicarboxylic acid, **4**. This corresponds to a concentration of 10 mg mL<sup>-1</sup>. <sup>e</sup> pK<sub>a3</sub> for enolic OH.



**Fig. 1** Bio-sourced compounds under study including amino acids, carboxylic acids and polyols. Platform chemicals are labeled with (P) and liquids (l).

in a variety of solvents, including water and supercritical carbon dioxide (scCO<sub>2</sub>). These data, to the best of our knowledge, have not been made available collectively elsewhere. In our work, attempts were not made in all cases to obtain absolute solubility values but rather to obtain data for practical purposes. A minimum arbitrary solubility level, potentially suitable for extractions or reactions using these green media, was chosen for each solvent system studied. These were 20 mg mL<sup>-1</sup> (liquid solvents), 1.7  $\mu$ L mL<sup>-1</sup> (liquids in CO<sub>2</sub>), 0.5 mg mL<sup>-1</sup> (solids in

CO<sub>2</sub>/MeOH) and 20 mg g<sup>-1</sup> (ionic liquid solvents). Although in some cases, *vide infra*, absolute data was obtained.

Water, being both abundant and benign, is a popular green solvent.<sup>15</sup> Its solvating properties can be altered through changes in pH, temperature, and pressure. All 14 compounds were examined for their solubilities in neutral deionized water, as well as acidic (acetate) and basic (ammonia) aqueous buffer solutions. Simple alcohols, namely methanol and ethanol, were also examined as they are less hazardous than more commonly used hydrocarbon, ethereal and chlorinated laboratory solvents. Table 1 summarizes the results of these studies. Researchers in the field of green chemistry frequently analyse samples from reaction mixtures using either NMR or GC-MS techniques. Furthermore, products are often extracted from aqueous phase reactions using chlorinated or ethereal solvents. Therefore, data for chloroform and diethyl ether are also reported.

Examination of these solubility data revealed several trends. As one might expect from the partition coefficient values for such compounds, the majority of the tested compounds proved soluble in neutral water. However, **4** and **5** were insoluble, possibly as a result of available resonance forms of their conjugate bases that are not accessible for the other acids (**6–10**). Also, the amino acids, glutamic acid, **2**, and aspartic acid, **3**, did not to dissolve in neutral water after 24 h. These compounds were also insoluble in the alcohols and organic solvents examined. pH was expected to have a notable influence on the solubilities of these amino acids. Indeed, all of the amino acids studied were soluble in the basic buffer solution (where they would exist as negative ions), as were all other studied compounds. The acidic buffer solution was successful in dissolving **3** but not **2**. Curiously, the only other compound to be found insoluble in the acidic buffer was tartaric acid, **7**. It should be noted that the predicted partition coefficient for **7** indicates a higher degree of hydrophilicity (more similar to the amino acids) for this carboxylic acid compared with the

**Table 2** Specific solubilities of various compounds at room temperature

Compound	Solvent	Solubility (g/g)	Reference
1	Water	1.1 (30 °C)	17
2	Water	0.023	18
3	Water	0.00785	19
4	Water	0.001	SRC <sup>a</sup>
4	MeOH	0.012	<i>This work</i>
5	Water	0.00808	20
5	EtOH	0.0457	20
6	Water	0.1	MSDS <sup>c</sup>
6	MeOH	0.68 <sup>b</sup>	<i>This work</i>
6	EtOH	0.38 <sup>b</sup>	<i>This work</i>
7	Water	1.33	MSDS <sup>c</sup>
7	MeOH	0.59	MSDS <sup>c</sup>
7	EtOH	0.33	MSDS <sup>c</sup>
7	CHCl <sub>3</sub>	Insoluble	MSDS <sup>c</sup>
8	Water	0.56 (20 °C)	MSDS <sup>c</sup>
8	MeOH	0.83 (20 °C)	MSDS <sup>c</sup>
8	EtOH	0.46 (20 °C)	MSDS <sup>c</sup>
8	Et <sub>2</sub> O	0.0084 (20 °C)	MSDS <sup>c</sup>
9	Water	0.111 (31 °C)	21
9	CHCl <sub>3</sub>	0.000933 (29 °C)	21
12	Water	1.8	22
12	EtOH	0.00801	23
13	Water	1.79	24

<sup>a</sup> SRC PhysProp Database. <sup>b</sup> Spontaneous decarboxylation occurs at concentrations greater than these. <sup>c</sup> Material Safety Data Sheets (MSDS) listed solubility data for some compounds in various solvents.

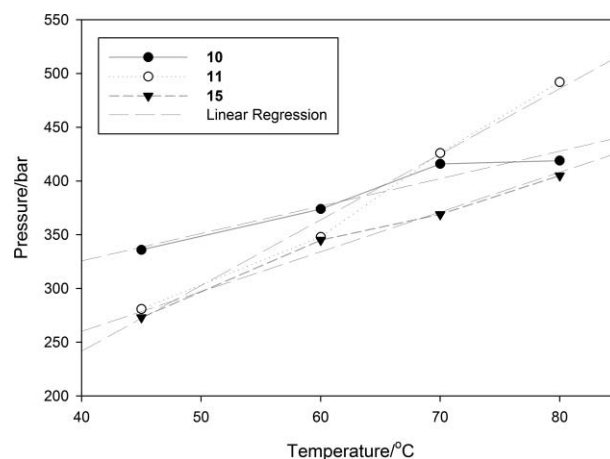
other carboxylic acids (**4–6**, **8–10**) in this study. The behaviour of **7** could prove useful for reactions carried out in water, where tartaric acid could be precipitated out of solution simply by acidification. To summarize, all 14 compounds studied in this work can be made readily soluble in water, simply by adjusting the pH appropriately.

Each of the carboxylic acid and ester containing compounds (**4–11**) was found to be soluble in methanol, with the exception of the amino acids, **1–3**. The sugar alcohols, **12–14**, were also insoluble in methanol. All of the methanol-soluble compounds were also soluble in ethanol with the exception of 2,5-furandicarboxylic acid, **4**, which took a long time to dissolve in methanol. The only compounds that were soluble in chloroform and diethyl ether were the liquids, **10** and **11**. This data reflects the weaker intermolecular interactions within **10** and **11**, their moderate strength within **5–9** and their greater strength within **4**. This is apparent when the melting points of these compounds are considered; **4**,  $T_m$  342 °C > **5**,  $T_m$  287 °C > **9**,  $T_m$  185 °C > **7**,  $T_m$  171 °C > **6**,  $T_m$  161 °C > **8**,  $T_m$  139 °C > **10**,  $T_m$  33 °C > **11**,  $T_m$  -43 °C.

While we did not set out to obtain specific and accurate solubility measurements, we recognize that such data would be valuable and, as such, have included a brief overview of these values as presented in the literature (Table 2). These data are, on the whole, comparable with the results presented in Table 1. However, it should be noted that in some cases where we were unable to observe noticeable dissolution, minute quantities have been reported as soluble in the literature (*e.g.* **9** in chloroform).<sup>21</sup> In addition, we carried out our own specific solubility experiments on a number of compound/solvent combinations for which we were unable to obtain literature values. For **4** in methanol, we observed a solubility of 0.0120

(± 0.0015) g/g. This was somewhat higher than expected given the low levels of aqueous solubility reported in databases for this compound. The solubility of **6** was also assessed in ethanol and methanol. While we were able to dissolve a large proportion of the solid (>2.7 g in 5 mL MeOH, >1.5 g in 5 mL EtOH), the solutions began frothing with subsequent additions of solid. We attributed this to the spontaneous decarboxylation of oxalacetic acid under sufficiently acidic conditions.<sup>16</sup>

After studying solubility in water, alcohols and organic solvents, the phase behaviour of **10** and **11** in scCO<sub>2</sub> was investigated. The low viscosity and high diffusivity of scCO<sub>2</sub> make it a promising reaction solvent.<sup>25</sup> However, of the compounds studied only the two liquid samples (**10**, b.p. 30 °C/0.3 mmHg, **11**, b.p. 100 °C/0.3 mmHg) demonstrated appreciable solubility in pure scCO<sub>2</sub> (Fig. 2), due to their weaker intermolecular interactions compared with the other twelve compounds studied. For **10** and **11**, the mole fraction solubility,  $y$ , was determined as 0.00342 ( $y \times 10^3 = 3.4$ ) and 0.00810 ( $y \times 10^3 = 8.1$ ) respectively. These are appreciable levels of solubility that are comparable with many organic molecules reported in the literature (acetyl salicylic acid and atropine), but significantly lower than small molecules such as acetic acid and acetonitrile.<sup>26</sup> None of the other compounds from Fig. 1 were soluble in neat CO<sub>2</sub>. Due to the production of 5-hydroxymethylfurfural, **15**, in the chemical conversion of many sugars,<sup>7</sup> we decided to study its phase behavior in carbon dioxide as well. While **15** is a solid at room temperature (unlike **10**, **11**), its melting point is around 30 °C and so it is actually a liquid at all temperatures studied, and therefore its phase behaviour should be comparable. At low temperatures, it demonstrated behavior similar to **10**, while at temperatures of 70 °C and higher its phase behavior was similar to that of **11**. Its mole fraction solubility was calculated to be 0.00565 ( $y \times 10^3 = 5.7$ ). As such, if a mixture of **10** and **15** were to be produced in a reaction, as is sometimes the case,<sup>27</sup> scCO<sub>2</sub> would not be a good choice for separation. However, if either product was produced selectively and in good yield in a reaction (*e.g.* acid-catalysed dehydration of glucose or fructose in an ionic liquid medium), scCO<sub>2</sub> would be a good choice for the extraction process.



**Fig. 2** Temperature–pressure phase diagram for levulinic acid, **10**,  $\gamma$ -hydroxybutyrolactone, **11** and 5-hydroxymethylfurfural, **15** in neat carbon dioxide. Error bars are omitted for clarity, pressure ± 0.3 to 2.1 bar.

**Table 3** Solubility of xylitol, **12**, and D-xylose, **16** in ILs<sup>a</sup>, in comparison to solubilities of 6-carbon sugars

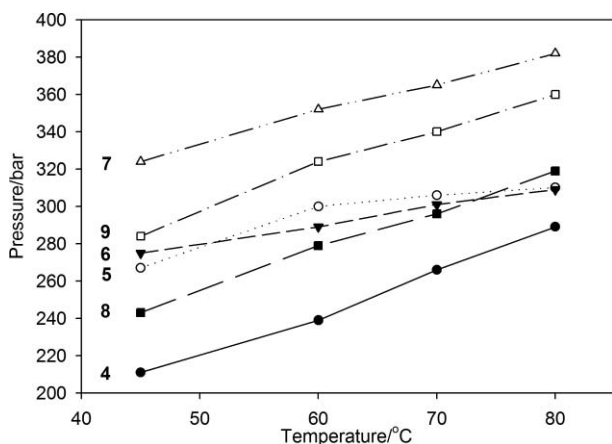
IL	Solubility <sup>b</sup> at 100 °C (g/g)		IL	Solubility at 30 °C (g/g) <sup>29</sup>	
	<b>12</b>	<b>16</b>		Glucose	Fructose
[PR <sub>4</sub> ]DBS	Not soluble	0.1294 ± 0.0085	[PR <sub>4</sub> ]Cl	0.0469	—
BMImpPF <sub>6</sub>	0.0244 ± 0.0095	0.0230 ± 0.0035	BMImpPF <sub>6</sub>	< 0.0004	—
BMImpCl	0.1529 ± 0.0083	0.0820 ± 0.0275	BMImpCl	—	0.5233
ChoCl/oxalic acid	0.0290 ± 0.0014	0.0658 ± 0.0067			
ChoCl/citric acid	0.0378 ± 0.0055	Not soluble			

<sup>a</sup> ILs prepared using literature procedures and rigorously dried.<sup>3b,33</sup> ChoCl is choline chloride. <sup>b</sup> This work.

A second set of experiments was performed using methanol (3 mL, 10% by volume,  $x = 0.127$ ) as a co-solvent. All of the compounds previously found to be soluble in methanol, Table 1, were tested in this scCO<sub>2</sub>/MeOH medium. Fig. 3 outlines the results of these analyses. For **4–9**,  $\gamma$  was determined as  $5.9 \times 10^{-4}$  (**4**),  $9.1 \times 10^{-4}$  (**5**),  $6.4 \times 10^{-4}$  (**6**),  $5.6 \times 10^{-4}$  (**7**),  $6.5 \times 10^{-4}$  (**8**) and  $4.0 \times 10^{-4}$  (**9**). Surprisingly compound **4** was found to be the most soluble requiring less dense (lower P) CO<sub>2</sub> to maintain a single phase. **5** and **6**, despite having the same number of carboxyl groups as **4**, are less soluble. We can attribute this to their increased flexibility, allowing for conformational changes which may favor inter- and/or intramolecular H-bonding and therefore disfavour dissolution. The least soluble compound, **7**, possesses a large number of hydroxyl and carboxylic acid groups, and retains a reasonably high degree of flexibility and therefore intra- and intermolecular forces would be difficult to overcome. Overall, the observed trends correlate well with the intermolecular bonding within these compounds. To complete this study and confirm that ethanol would also make an appropriate co-solvent in such systems, **9** was studied in scCO<sub>2</sub>/EtOH (10% EtOH by volume, 17 mg,  $x = 0.091$ ). Cloud points were observed at all four temperature points: 45 °C, 179 ± 7.9 bar; 60 °C, 214 ± 4.1 bar; 70 °C, 265 ± 4.3 bar; 80 °C, 293 ± 3.3 bar. These cloud points were generally less distinct than those observed with methanol, but it is worth noting that lower pressures were needed to achieve a homogeneous solution at each temperature. In summary, the experiments performed clearly show that scCO<sub>2</sub>/alcohol

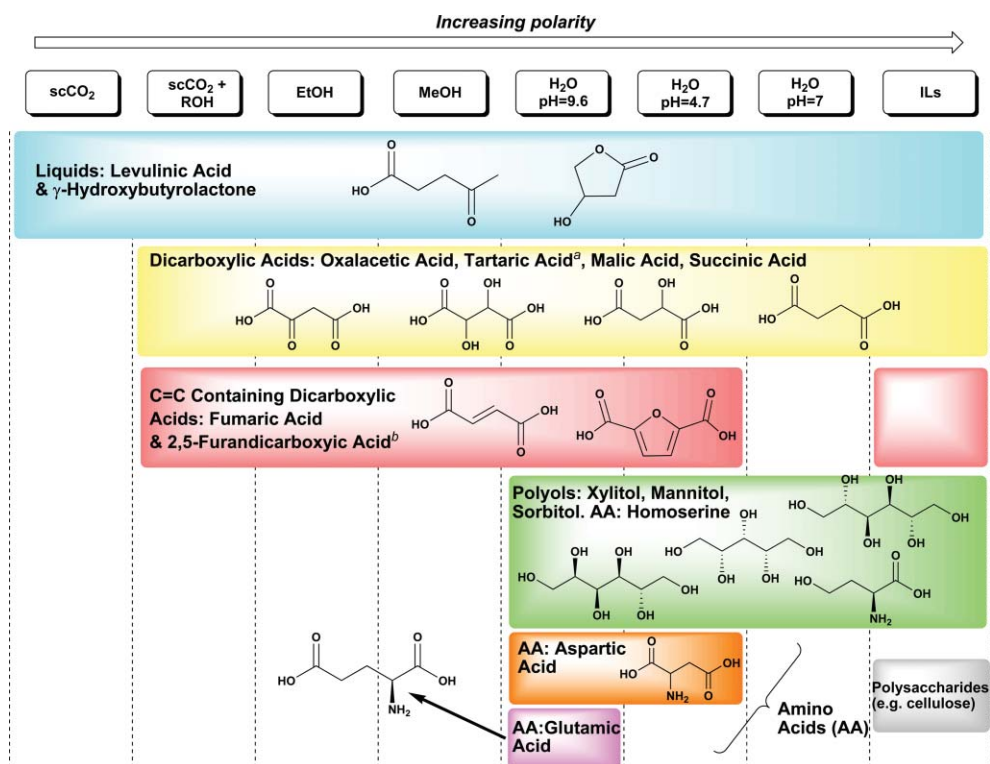
mixtures would be useful media for investigating the chemistry of compounds **4–11**.

Our most recent solubility work has been with room temperature ionic liquids (ILs). ILs consist entirely of ions, have melting points below 100 °C, and exhibit no detectable vapour pressure below the temperature of their thermal decomposition.<sup>28</sup> They are very versatile, with the potential for tuning of various properties such as polarity, conductivity, density, melting point, and solvent capacity.<sup>29,30</sup> Detailed studies on the solubility of carbohydrates in ionic liquids and their extraction from aqueous solution has recently been published.<sup>29,31</sup> In our work, a representative compound from each class studied (**2**, **5**, **7**, **9** and **12**) were screened for solubility in the commercially available, hydrophobic IL tetradecyl(triethyl)phosphonium dodecylbenzenesulfonate ([PR<sub>4</sub>]DBS). 10 mg of the compound and 500 mg of the IL were combined in a small vial, which was capped and left to stir overnight. **5** and **9** dissolved under these conditions to yield solutions with concentrations of 20 mg g<sup>-1</sup>, while **2**, **7**, and **12** did not. These three samples were then heated to 100 °C in a water bath and stirred for 1 h. **2** and **12** remained undissolved whereas **7** dissolved. Focusing in on xylitol, **12**, and its precursor sugar D-xylose, **16**, solubility tests were carried out with several other ILs,† the results of which are presented in Table 3. The specific solubility of each compound was determined by the addition of small amounts of solid to a vial of the IL, stirred continuously at 100 °C, in 2 h intervals until it no longer dissolved. **12** was found to be most soluble in BMImpCl, while **16** was most soluble in [PR<sub>4</sub>]DBS. Both exhibited less solubility than fructose in BMImpCl, but greater solubility than glucose in BMImpPF<sub>6</sub>.<sup>29</sup> Such results are promising for the use of xylitol and D-xylose as bio-feedstocks in green reactions, as many transformations of 6C-sugars (e.g. glucose and fructose) in ILs have recently been reported.<sup>32</sup> Finally, it should be noted that our observed solubility of xylose in BMImpPF<sub>6</sub> was found to be slightly lower than the recently published experimental value of 0.0280 g/g.<sup>31</sup>



**Fig. 3** Temperature–pressure phase diagram for bio-sourced carboxylic acids **4–9** in carbon dioxide/methanol. Error bars are omitted for clarity, pressure ± 0.3 to 3.4 bar.

† Due to the lack of commercial availability and associated cost, it was deemed impractical to purchase a large variety of ionic liquids for screening. As such, ionic liquids which were already available in the lab ([PR<sub>4</sub>]DBS, BMImpCl, BMImpPF<sub>6</sub> – in use by a co-worker on another project) were used. The eutectic mixtures (ChoCl/citric acid, ChoCl/oxalic acid) were selected because they could be easily made from commercially available, benign reagents. While not technically ionic liquids, eutectic mixtures share many of the same properties of ionic liquids, and it is not uncommon to group the two types of solvent together in a single class.



**Fig. 4** Schematic representation of the degree of solubility of classes of bio-sourced molecules in various 'green' solvents. <sup>a</sup>Not soluble at pH 4.7. <sup>b</sup>Not soluble in EtOH.

## Conclusions

Analysis of the solubilities of these bio-sourced feedstocks has led to the discovery of several trends, and enabled the grouping of these compounds accordingly (Fig. 4). The two liquid samples studied, **10** and **11**, exhibited universal solubility over the entire range of 'green' solvents examined. Furthermore, **15** is also soluble in scCO<sub>2</sub> and provides a useful working hypothesis that bio-sourced molecules with low melting points (at or below 30 °C) will dissolve in this green solvent. The dicarboxylic acids, **6–9**, proved to be the next most soluble group of compounds, being soluble in all media except neat scCO<sub>2</sub>. The acids containing C–C double bonds, **4** and **5**, were also widely soluble and demonstrated solubilities comparable to that of the previous group, except in the case of neutral water. The polyols, **12–14** (and homoserine, **1**) displayed aqueous solubility over a range of pHs, and were also found to be soluble in ILs. Finally, the amino acids (**2** and **3**) showed the smallest span of solubility, being insoluble in all the solvents studied, except for water, and even then only with modified pH. Of course, **2** and **3** may be soluble in different ionic liquids not used in this work. While they were not studied during the course of our work, we have included polysaccharides in a summary diagram (Fig. 4) as they are important feedstocks. Studies performed over the past decade have shown that such biopolymers can be dissolved and reacted in suitable ionic liquid systems.<sup>34</sup> They join the amino acids at the bottom of the hierarchy, as one of the least widely soluble classes of bio-sourced molecules/materials (particularly cellulose, lignin and chitin).

In summary, we present several sets of data outlining the solubility of bio-sourced feedstocks in various green solvents. Such information could provide valuable insight into the workability of a host of new, green reactions using these compounds, opening the door to a realm of more environmentally friendly procedures

## Experimental

L-Glutamic acid (99%), L-tartaric acid (99%), DL-aspartic acid (99%), DL-malic acid (99%) and cell culture tested fumaric acid were obtained from Sigma-Aldrich. Homoserine, furan-2,5-dicarboxylic acid, oxalacetic acid, levulinic acid, xylitol, D-sorbitol, anhydrous citric acid, anhydrous oxalic acid, and choline chloride were all purchased from Alfa Aesar in 98% or greater purity.  $\gamma$ -Hydroxybutyrolactone was also acquired from Alfa, but in 96% purity. Mannitol (>99%) and D-xylose (>99%) were obtained from ACP Chemical Inc. and Acros Organics, respectively.

In determining specific solubilities for **4** in methanol and **6** in methanol and ethanol, small amounts of the compound were added to a vial containing 5 mL of the solvent, followed by mixing and at least 10 min to equilibrate. This procedure was repeated until the solid no longer dissolved fully.

For the scCO<sub>2</sub> experiments, a SFT-Phase Monitor II instrument (Supercritical Fluid Technologies Inc.) was used to record cloud point pressures at four different temperatures. For the first set of experiments, a known amount of compound (0.05 mL **10**, 0.10 mL **11**, and 0.0966 g **15**) was placed into the view cell,

which was then sealed and filled with liquid CO<sub>2</sub> (30 mL). The system was then brought up to the desired temperature and allowed to equilibrate for 20 min then the pressure was adjusted until a cloud point was observed (as monitored via a CCD camera and a computer screen). The pressure was then increased by 50–100 bar and lowered again more slowly to confirm the previous reading. This procedure was repeated at least once more (depending upon how distinct a cloud point was observed). For the second set of experiments, a known amount of compound (10–20 mg) was dissolved in 3 mL of methanol and placed into the view cell (30 mL in volume), the cell was sealed and filled with liquid CO<sub>2</sub> and then observed under varying temperature and pressure conditions, as described above.† Errors in the cloud point data were typically 0.3 to 2.1 bar for neat scCO<sub>2</sub> and 0.3 to 3.4 bar for scCO<sub>2</sub>/MeOH.

## Acknowledgements

We would like to thank Mr Zhenzhong Hu for his translation of ref. 21. We also thank Memorial University, NSERC of Canada (Discovery Grant–FMK, Postgraduate Scholarship–SMP), the Provincial Government of Newfoundland and Labrador (IRIF grant–FMK, Resource Development Scholarship–SMP) and Canada Foundation for Innovation (Leaders Opportunity Fund Award) for generous funding.

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