

Article

Enhanced solubility of lignin monomeric model compounds and technical lignins in aqueous solutions of deep eutectic solvents

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ACS Sustainable Chem. Eng., **Just Accepted Manuscript** • DOI: 10.1021/acssuschemeng.7b00053 • Publication Date (Web): 05 Apr 2017Downloaded from <http://pubs.acs.org> on April 7, 2017**Just Accepted**

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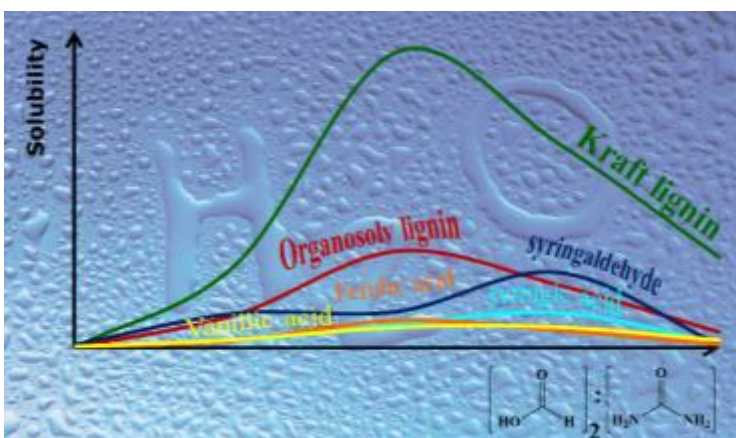
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38 *ABSTRACT.* The solubilities of lignin monomeric model compounds and technical lignins
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40 (organosolv and kraft) in aqueous solutions of several deep eutectic solvents (DES) were here
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42 investigated. The effects of DES components, temperature and concentration, were evaluated. The
43
44 results show aqueous solutions of DES to be a new class of powerful solvents where both the
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46 hydrogen bond donor and the hydrogen bond acceptor synergistically contribute to increase the
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48 solubility of the lignin model compounds, being the dispersive interactions with lignin the driving
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50 force behind the good performance of DES. The solubility of the model compounds is shown to
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52 be a good guide for the selection of the best DES for technical lignins solubility, leading to
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54 identifying an aqueous solution of DES allowing a solubility enhancement of 1181.7 ± 29.2 and
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3 228.5 ± 9.7 times for kraft and organosolv lignin, respectively. The results indicate that the
4 solubility of the technical lignins and their monomers in DES aqueous solutions is driven by a
5 hydrotropic mechanism, here confirmed by dynamic light scattering that is here observed for the
6 first time with DES as hydrotropes.
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14 TOC GRAPHIC.



34 KEYWORDS. Deep eutectic solvents (DES); DES aqueous solutions; solubility; lignin
35 monomeric model compounds; organosolv lignin; kraft lignin; biorefinery; hydrotropy.
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41 SYNOPSIS. Aqueous solutions of DES enhance the solubility of technical lignins more than 200
42 times opening the possibility for new lignin extraction and conversion processes.
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INTRODUCTION

Lignocellulosic biomass is an abundant renewable source of raw materials in a sustainable economy context. Its fractionation and the processing of its constituents is of major importance for its exploitation.¹ The fractionation involves the removal of lignin to yield a rather pure cellulosic substrate. Lignin is thus a by-product from pulping processes exceeding 70 million tonne per year, which is mostly used for power generation.² Its abundance and unique structural features, could lead to enhanced valorization as a source of added value materials and chemicals. However, due to its structural heterogeneity and the lack of efficient conversion processes, only 2 % of the available lignin is being used in some low volume, niche applications.^{2,3} Native lignin is a three-dimensional phenolic polymer composed of three sub-unit types, p-hydroxyphenyl, guaiacyl and syringyl (Figure S 1, at Supporting Information), linked together through aryl ether (β -O-4, α -O-4, 4-O-5) and carbon-carbon bonds (5-5', β -5, β -1, β - β).⁴ The wood species, the delignification processes and the recovery approaches from pulping liquors all have a remarkable influence on the structure of the isolated lignin. Thus the structural characteristics of isolated lignin have an influence on its performance towards further processing and determine its suitability for different applications.⁵⁻⁷ There has been a growing interest in the conversion of lignin into value-added aromatic compounds including aldehydes and acids by thermochemical processes^{8,9} considering their increased demand for food and personal care products, and as a intermediates in the synthesis of fine chemicals.¹⁰ However, the availability of an adequate solvent for lignin is hampering the successful development of most of these processes and applications. The development of new breakthrough technologies, aiming at enhancing value and reducing the CO₂ emissions, is the main objective of the pulp and paper sector to achieve a European low-carbon bio-economy by 2050.¹¹ Deep eutectic solvents (DES), and their natural counterparts (natural deep eutectic solvents -

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3 NADES), have been considered one of the most promising approaches for new pulping
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5 technologies.¹²
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8 DES were introduced by Abbott and co-workers, in 2003.¹³ They are composed of two or three
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10 low-cost components capable of associating with each other through hydrogen bond interactions,
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12 to form an eutectic mixture with a melting point much lower than those of the pure components.¹³
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15 One of the most widespread hydrogen bond acceptors (HBA) used for the preparation of DES is
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17 choline chloride ([Ch]Cl). It can form DES in combination with hydrogen bond donors (HBD)
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19 such as urea, glycerol, carbohydrate-derived polyols¹⁴ or renewable carboxylic acids.¹⁵ Since 2003,
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21 there has been an increasing number of works concerning DES as potential solvents for lignin.^{16–}
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25 ¹⁹ However, often pure DES are highly viscous raising problems in their application. The
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27 possibility of using aqueous solutions of DES to fractionate biomass is very attractive but yet
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29 poorly explored.
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32 Hydrotropes are compounds used to increase the concentration levels of hydrophobic solutes in
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34 aqueous solutions. They are a class of water soluble compounds characterized by an amphiphilic
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36 structure. Neuberg²⁰ was the first to propose this concept by demonstrating that the solubility of
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38 sparingly soluble compounds in water could be enhanced by the addition of alkali metal salts of
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40 various organic acids with short alkyl chains. Albeit a large body of work during the past century
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42 addressed this phenomenon, its mechanism of action has been poorly understood. Recent studies^{21–}
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44 ²⁸ proposed the co-aggregation of the solute with the hydrotropes to be the main mechanism behind
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46 the enhanced solubilization observed. Although hydrotropes have been used since long in
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48 formulation of drugs, cleaning agents and personal care products,^{29–32} their application to biomass
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50 treatment ^{33,34,35} has been scarce. Yet they seem to hold a lot of potential to be applied on this field
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53 where novel, greener, and more performant solvents are in great demand.
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To assess the potential of DES as new solvents for the delignification process, and subsequent use of lignin, it is important to study the dissolution of lignin in neat DES and their aqueous solutions. Aiming at select the best DES to be used as delignification media, the solubility of monomeric lignin model compounds (syringaldehyde, and syringic, vanillin and ferulic acids) in aqueous solutions of DES was investigated. The effects of DES components (chemical structure and HBD:HBA molar ratio), temperature and concentration, were investigated. This study was used to assess the transferability of the information based on these studies with lignin monomers to real lignin samples and to identify the best DES for the dissolution of technical lignins (organosolv and kraft). This work intends to contribute to achieve a deeper and sounder knowledge of the solubility of lignin in aqueous solutions of DES opening new perspectives for future delignification and lignin conversion processes.

EXPERIMENTAL SECTION

Chemicals. Several combinations of HBDs and HBAs were used to prepare deep eutectic solvents and were studied in this work to cover the effects of the HBD, HBA and HBD structure on the solubility of lignin monomeric model compounds. In this work urea was used as both HBD and HBA, as demonstrated by Ashworth *et al.*³⁶ Aiming to guarantee the correct molar proportion in the preparation of DES, the water content of all starting materials was measured using a Metrohm 831 Karl-Fisher coulometer. The key information about the HBDs and HBAs used is summarized in Table 1, and their structures shown in Figure 1.

Table 1. Compound descriptions, CAS number, molecular weight, mass fraction purity, water content and supplier of the DES components investigated

Compound	CAS number	Mw / g mol ⁻¹	Purity ^a / wt %	Water Content / wt %	Supplier
Hydrogen Bond Donor					
Formic acid (FA)	64-18-6	46.03	98	1.08 ± 0.08	Panreac
Acetic acid (AA)	64-19-7	60.05	99	0.12 ± 0.01	Fisher Scientific
Propionic acid (PA)	79-09-4	74.08	>99	0.09 ± 0.01	Merk Chemicals

L(+)-Lactic acid (LA)	79-33-4	90.08	88-92	14.5 ± 0.06	Riedel de Haën
Glycolic acid (GlyA)	79-14-1	76.05	99	0.11 ± 0.01	Acros Organics
DL-Malic acid (MA)	617-48-1	134.09	99.5	0.01 ± 0.00	Panreac
p-Toluenesulfonic acid monohydrate (PTSA)	6192-52-5	190.22	>98.5	2.63 ± 0.02	Sigma-Aldrich
Urea (U)	57-13-6	60.06	>99	0.003 ± 0.00	Panreac
Glycerol (G)	56-81-5	92.09	99.8	0.13 ± 0.04	Fisher Scientific
Ethylene glycol (EG)	107-21-1	62.07	>99.5	0.12 ± 0.02	Sigma-Aldrich
α -D(+)-Glucose (Glu)	492-62-6	180.16	96	anhydrous	Sigma-Aldrich
D(+)-Xylose (Xyl)	58-86-6	150.13	99	0.01 ± 0.00	Sigma-Aldrich
D(-)-Fructose (Fru)	57-48-7	180.16	98	0.25 ± 0.04	Panreac
Hydrogen Bond Acceptor					
Choline Chloride ([Ch]Cl)	67-48-1	139.62	99	2.17 ± 0.45	Acros Organics
L(-)-Proline (Pro)	609-36-9	115.13	99	3.95 ± 0.61	Acros Organics
Betaine (Bet)	107-43-7	117.15	98	1.27 ± 0.11	Acros Organics
Urea (U)	57-13-6	60.06	>99	0.003 ± 0.00	Panreac

^a as reported by the supplier.

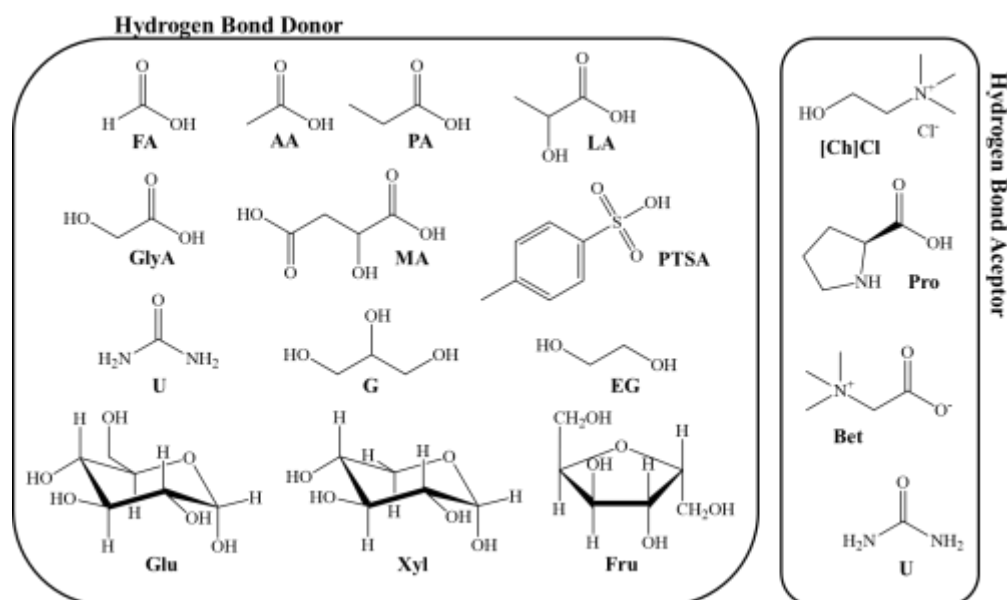


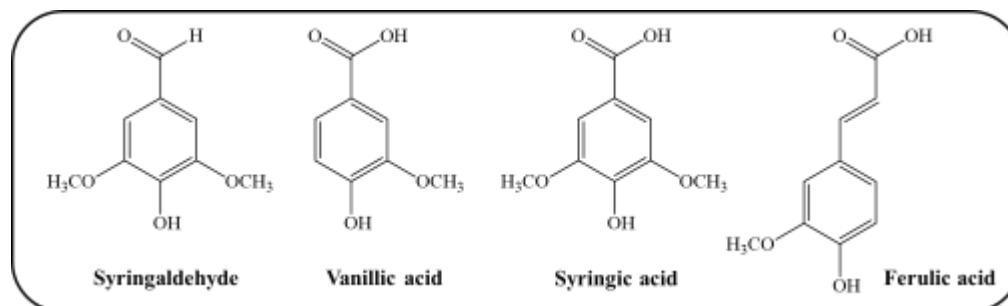
Figure 1. Chemical structures of investigated HBDs and HBAs.

Lignin monomeric model compounds, such as, syringaldehyde, and vanillic, syringic and ferulic acids were selected in this work to study the potential of DES (neat or in aqueous solution) for lignin solubilization, taking into account that these monomeric aromatic compounds are lignin depolymerization products, e.g. by thermochemical processes.^{8,9,37} The key information about these compounds is summarized in Table 2, and their structures are shown in Figure 2.

Table 2. Lignin monomeric model compounds information: name, CAS, molecular weight, mass fraction purity and supplier

Lignin monomeric model compounds	CAS number	Mw / g mol ⁻¹	Purity ^a / wt %	Supplier
Syringaldehyde	134-96-3	182.17	98	Acros Organics
Vanillic acid	121-34-6	168.15	97	Acros Organics
Syringic acid	530-57-4	198.17	>98	Acros Organics
Ferulic acid	1135-24-6	194.18	>99	Acros Organics

^a as reported by the supplier.

**Figure 2.** Chemical structures of lignin monomeric model compounds investigated.

Two samples of technical lignins were selected to study the solubilization of lignin in aqueous solution of DES. A lignin produced by ethanol organosolv process from *E. globulus* wood (kindly supplied by Lignol Innovations, Canada) and a lignin isolated from *E. globulus* industrial kraft liquor (kindly supplied by The Navigator Company, Portugal). According to Costa *et al.*,⁷ after the depolymerization process these technical lignin samples presented syringaldehyde, vanillin, syringic and vanillic acids and p-hydroxybenzaldehyde as degradation products. All the lignin monomeric model compounds and lignin sample were used as received. The chemical structures of the lignin monomeric model compounds are depicted in Figure 2.

DES preparation. The DES families investigated in this study (carboxylic acids, polyols and sugars) are presented in Table 3. The two-component mixture (HBD and HBA), were placed in sealed glass vials with a stirring bar and heated in an oil bath at 323.15 ± 0.01 K, with constant stirring until a transparent liquid was formed. After the liquid formation, the mixture was kept at this temperature for one hour before being allowed to return to room temperature.¹⁵ All experiments were carried out with DES liquid at room temperature. The aqueous solutions of DES

(25, 50, 75 and 95 wt %) were prepared by diluting the neat DES in deionized water. The water content of the DES precursors was checked using a Metrohm 831 Karl Fisher coulometer and the value was taken into account in the preparation of the DES aqueous solutions. The pH of DES aqueous solutions was measured at 298.15 ± 0.01 K using a Mettler Toledo S47 SevenMulti™ dual meter pH and conductivity equipment with an uncertainty of ± 0.01 . The calibration of the pH meter was carried out with two buffers (pH of 4.00 and 7.00).

Table 3. List of DES families used in this study

DES families	Molar ratio
Carboxylic acids	
FA:[Ch]Cl	2:1
AA:[Ch]Cl	2:1
AA:Pro	2:1
AA:Bet	2:1
AA:U	4:1
PA:[Ch]Cl	4:1; 3:1; 2:1; 1:1; 1:2; 1:3; 1:4
PA:Pro	2:1
PA:Bet	2:1
PA:U	4:1; 2:1; 1:1; 1:2; 1:4
LA:[Ch]Cl	2:1; 1:2
LA:Pro	2:1
LA:Bet	2:1
LA:U	2:1
GlyA:[Ch]Cl	3:1
GlyA:Pro	3:1; 2:1; 1:1
MA:[Ch]Cl	1:1
PTSA:[Ch]Cl	1:1
Polyols	
G:[Ch]Cl	2:1
EG:[Ch]Cl	2:1
Sugars	
Glu:[Ch]Cl	1:1
Xyl:[Ch]Cl	2:1
Fru:[Ch]Cl	1:1
Reference ¹³	
U:[Ch]Cl	2:1

Solubility of lignin monomeric model compounds. Each lignin monomeric model compound (syringaldehyde, and vanillic, syringic and ferulic acids) was added in excess amount to 2.0 ± 0.1 g of each DES aqueous solution, pure water and pure DES. They were then equilibrated at a given

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3 temperature (303.15, 313.15 and 323.15 K) under constant agitation (300 rpm) using a stirring
4 plate with heat control Pt1000, H03D series from LBX Instruments and an specific aluminum disk
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6 to support the sealed glass vials with a stirring bar. After the saturation was reached, the samples
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8 were filtered with 0.45 μm PTFE filters from Whatman to separate the macroscopic solid from the
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10 liquid phase. After the filtration, all samples were collected and put in an air oven at the same
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12 equilibrium temperature for 2 hours. Then, the samples of the liquid phase were diluted in
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14 distilled water, and the amount of lignin monomeric model compounds was quantified by UV-
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16 spectroscopy using a SHIMADZU UV-1700, Pharma-Spec spectrometer at a wavelength of 307,
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18 256, 265 and 314 nm, respectively, using calibration curves (see Figure S 2 and Table S 1,
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20 Supporting Information). Note that, in some cases, the maximum absorbance of these compounds
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22 was shifted, due to the strong interaction between model compounds and DES. At least three
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24 individual samples were quantified for each mixture and temperature.
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32 **Solubility of technical lignins.** Similar to the procedure described above for the study of the
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34 solubility of lignin monomeric model compounds, technical lignins were added in excess amount
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36 to $2.0 \pm 0.1\text{g}$ of DES aqueous solutions, pure water or pure DES. Only the DES with the best
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38 performance on the solubility tests of lignin monomeric model compounds was evaluated for
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40 organosolv and kraft lignin solubility at 313.15 and 323.15 K. However, due to the dark color and
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42 high viscosity of the solutions, after saturation was reached in both pure DES and aqueous solution,
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44 it was not possible to filtrate or centrifuge the samples in order to separate the two phases. To
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46 overcome this limitation a method to quantify the dissolved lignin based on Fourier transform
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48 infrared spectroscopy developed by Soares *et al.*³⁸ was used. The analyses of the samples were
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50 carried out using a FT-IR system Spectrum BX, PerkinElmer, equipped with a single horizontal
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52 Golden Gate ATR cell (attenuated total reflectance), and a diamond crystal. All data were recorded
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3 at room temperature, in the range of 4000 - 600 cm^{-1} by accumulating 32 scans with a resolution
4 of 4 cm^{-1} and interval of 2 cm^{-1} . At least four individual samples were analyzed for each mixture
5 and temperature. After the spectra normalization and considering that lignin showed a band at
6 1594 cm^{-1} characteristic of aromatic skeletal vibration in FT-IR spectra,³⁹ the amount of lignin was
7 quantified using specific calibration curves (see Figure S 3 and Table S 2, Supporting Information).
8 When pure water was used, due to its low solubility, the amount of dissolved organosolv and kraft
9 lignins were quantified by UV-spectroscopy following the same methodology previously
10 presented, at a wavelength of 280 nm using the calibration curve of alkali lignin (see Figure S 2
11 and Table S 1, Supporting Information).
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24 **Dynamic light scattering.** To evaluate the presence of DES-solute nanoaggregates, as well as
25 to determine their size, saturated solutions of lignin model compounds and technical lignins in
26 aqueous solution of PA:U 2:1 at 50 wt % and 323.15 K were analyzed by dynamic light scattering
27 using a Malvern Zetasizer Nano-ZS from Malvern Instruments (zetasizer software version 7.12).
28 Samples were measured in disposable glass cuvettes at a temperature of 323.15 K. Data were then
29 acquired in the automatic mode, ensuring that enough photons were accumulated for the result to
30 be statistically relevant. At least two individual samples were analyzed in triplicated for each
31 sample and before the measurements, all samples were filtered with 0.45 μm PTFE filters from
32 Whatman. The aqueous solution of PA:U 2:1 at 50 wt % viscosity and refractive index at 323.15
33 K were previously measured by the DLS measurements.
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51 RESULTS AND DISCUSSION

52 Aiming at investigating the potential of aqueous solutions of DES in delignification processes, and
53 bearing in mind the complexity of lignin, the solubilities of some monomeric aromatic compounds
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such as syringaldehyde, and vanillic, syringic and ferulic acids were determined in aqueous solutions of DES. It is well known that the solubility of a substance fundamentally depends on the physical and chemical properties of the solute and solvent as well as on the temperature, pressure and on the pH of the solution. Considering that the DES properties depend on the HBD and HBA structures, it is crucial to evaluate the effects of HBDs and HBAs, their molar ratio, concentration in the aqueous solution, and temperature on the solubility of the lignin model compounds. In order to achieve this goal, the lignin model compound selected to develop this preliminary study was syringic acid, one of the main components of oxidatively depolymerized technical lignins.⁷ The solubilities of these lignin model compounds in pure water at 303.15, 313.15 and 323.15 K and at atmospheric pressure, were also measured for comparative purposes and are reported in Table 4.

Table 4. Experimental solubilities of lignin monomeric model compounds, organosolv and kraft lignins in pure water at atmospheric pressure

T/K	Solubility $\pm \sigma$ / mg g ⁻¹		
	303.15	313.15	323.15
Lignin and monomeric model compounds			
Syringaldehyde	2.92 \pm 0.01	4.41 \pm 0.10	7.91 \pm 0.76
Vanillic acid	1.81 \pm 0.06	2.93 \pm 0.06	3.24 \pm 0.11
Syringic acid	1.28 \pm 0.01	1.60 \pm 0.03	1.87 \pm 0.08
Ferulic acid	0.63 \pm 0.06	0.82 \pm 0.03	1.53 \pm 0.05
Organosolv lignin	-	0.93 \pm 0.17	1.07 \pm 0.24
Kraft lignin	-	0.64 \pm 0.002	0.79 \pm 0.009

σ , standard deviation.

Effect of DES components. Several families of DES were prepared combining HBD (carboxylic acids, polyols, sugars and urea (U)) with HBA ([Ch]Cl, Pro, Bet and U) at a molar ratio that results in a liquid DES at room temperature, aiming at studying the effects of HBDs and HBAs on syringic acid solubility. Therefore, in order to study the impact of the HBD on syringic acid solubility a series of DES with common HBA were used. Based on the well-known U:[Ch]Cl system,^{13,15} the favorable properties of [Ch]Cl, its low price and “green” characteristics overall,⁴⁰ this compound was adopted as the HBA for this study. Syringic acid solubility was studied in 25

wt % aqueous solution of DES (HBD:[Ch]Cl) at 303.15 K. The influence of HBD on the solubility enhancement of syringic acid and the respective pH of the DES aqueous solution are depicted in Figure 3. The detailed values of solubility and pH, and the respective standard deviations, are reported in Table S 3, at Supporting Information. On this figure the S and S_0 represent the solubility (mg g^{-1}) of syringic acid in the aqueous solutions of the DES and in pure water, respectively. Therefore, the S/S_0 ratio represents the solubility enhancement by the use of DES as solvent.

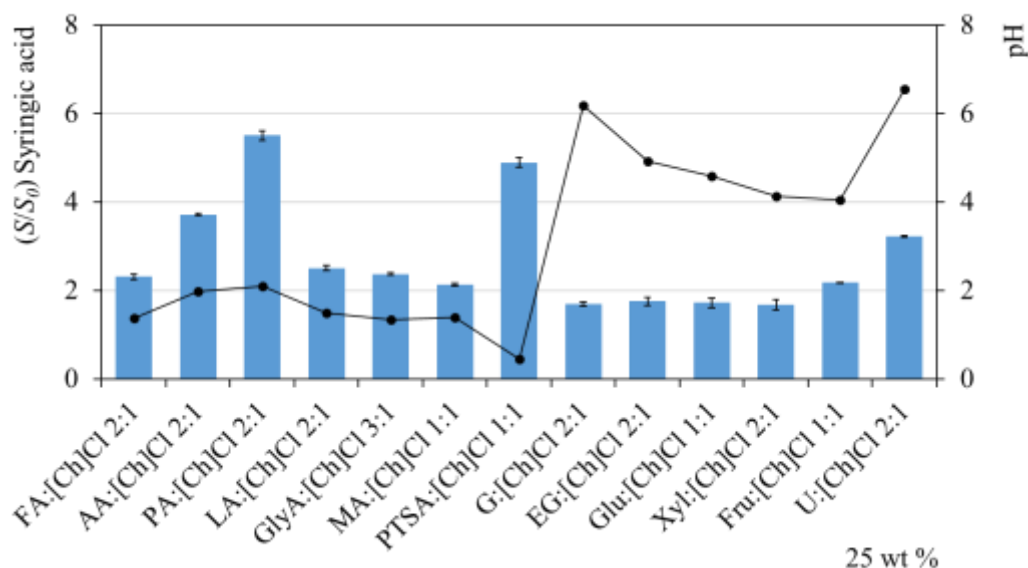


Figure 3. Influence of HBDs on the solubility enhancement of syringic acid in aqueous solutions with 25 wt % of DES, at 303.15 K. The pH value of the respective DES aqueous solutions is presented in black dots.

The results reported in Figure 3 show that the HBD chemical structure has a significant influence on the syringic acid solubility. Sugars and polyols-based DES exhibited a low ability to solubilize syringic acid, leading to a lower solubility enhancement (around 2-fold) than the U:[Ch]Cl reference DES (3-fold). A large number of hydroxyl groups on these HBDs makes them too polar and they probably form a network of hydrogen bonds that becomes a hindrance to syringic acid solubilization.⁴¹ A positive influence of carboxylic acids-based DES on syringic acid solubility was observed, with solubility enhancements that nearly reach 6-fold. Among the carboxylic acids-

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3 based DES, the PTSA and PA provided the best results (4.9 and 5.5-fold, respectively).
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5 Furthermore, it is perceptible that the alkyl side chain length has an impact over the syringic acid
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7 solubility as well as the presence or absence of functional groups on the acids chemical structure.
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10 As depicted in Figure 4, an increasing alkyl side chain length (from FA, to AA and PA) results in
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12 an increased solubility of the solute. The presence of hydroxyl groups in the acid alkyl chain of
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14 LA and GlyA was observed to have a negative impact in syringic acid solubility when compared
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16 with PA and AA, respectively. Similarly, LA demonstrated to have a better performance than MA.
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18 The presence of a second carboxylic group may be the reason for the lower solubilization
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20 performance of MA. Moreover, an enhanced performance of PTSA was expected due to the
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22 presence of the aromatic group and the possibility to establish $\pi\cdots\pi$ interactions with the aromatic
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24 ring of syringic acid. Although the PTSA was one of the best HBD, its performance was worse
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26 than that of the linear carboxylic acids.
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32 In general it seems that an increase in syringic acid solubility is achieved by decreasing the
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34 polarity of the carboxylic acids. These results suggest that the dispersive interactions between the
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36 organic acid alkyl chain and the syringic acid structure are the main reason for the good
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38 performance of PA, instead of the hydrogen bond interactions, $\pi\cdots\pi$ interactions and the polar
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40 character of polyols, sugars and some organic acids (LA, GlyA and MA). Furthermore, the pH of
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42 DES aqueous solutions seems to have no significant effect in the syringic acid solubility. Overall
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44 PA:[Ch]Cl with a molar ratio of 2:1 presented the best solubility enhancement.
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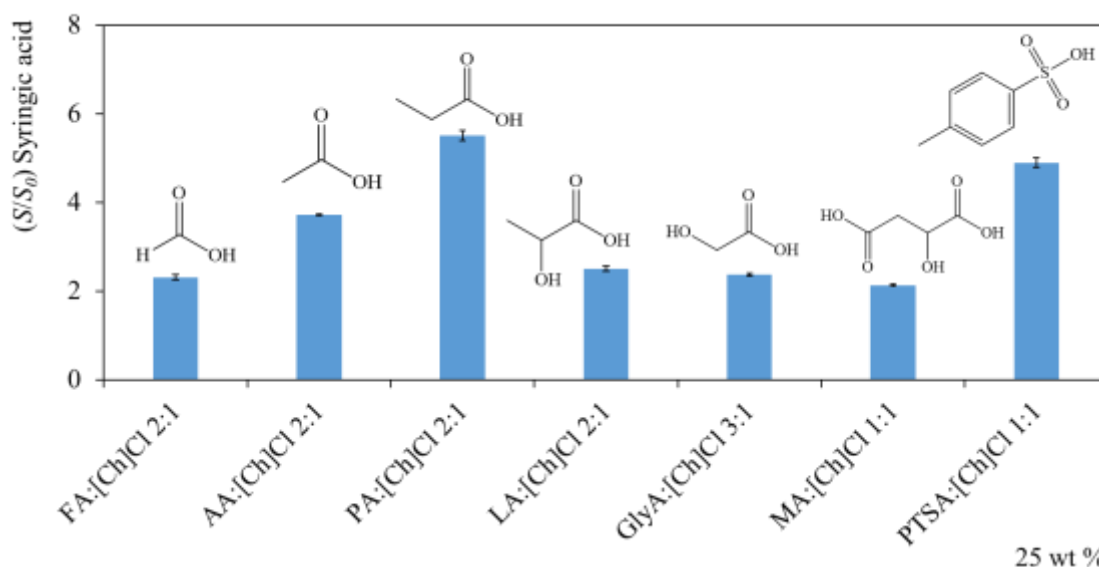


Figure 4. Influence of carboxylic acids HBDs chemical structure on the solubility enhancement of syringic acid in aqueous solutions with 25 wt % of DES, at 303.15 K.

Considering the advantageous performance of the carboxylic acids-based DES, three different carboxylic acids (LA, AA and PA) were combined with four HBAs ([Ch]Cl, Pro, Bet and U) in order to evaluate the effect of HBAs on syringic acid solubility. The solubility enhancement of syringic acid was again studied in 25 wt % aqueous solutions of DES at 303.15 K. The influence of HBA on the solubility enhancement of syringic acid and the pH of each DES aqueous solution are depicted in Figure 5. The detailed values of solubility and pH, and the respective standard deviations, are reported in Table S 3, at Supporting Information.

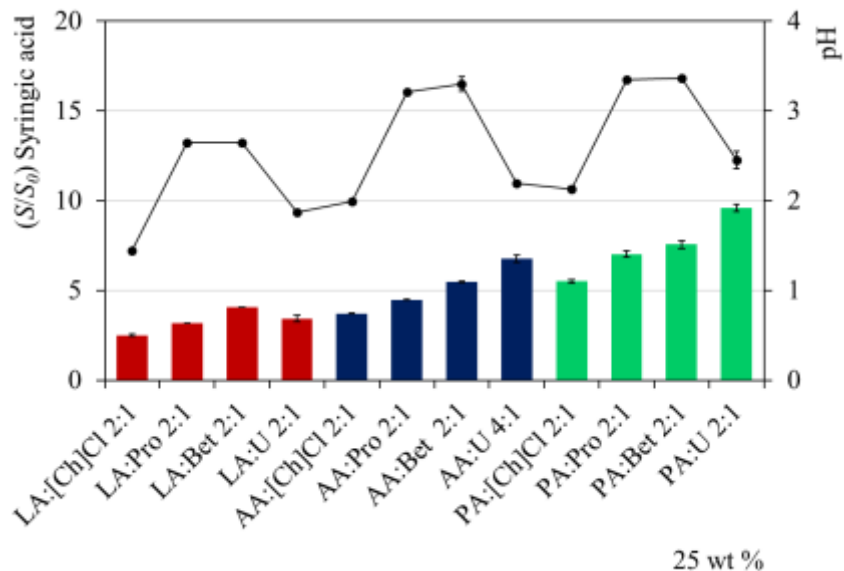


Figure 5. Influence of HBAs on the solubility enhancement of syringic acid in aqueous solutions with 25 wt % of DES, at 303.15 K. The pH value of the respective DES aqueous solutions is presented in black dots.

The results reported in Figure 5 show that the solubility of syringic acid is also affected by the HBAs, increasing in the sequence of [Ch]Cl < Pro < Bet < U, independently of the carboxylic acids studied, with the exception of LA. In this case, Bet showed a somewhat better syringic acid solubility enhancement (4-fold) than U (3.4-fold) as HBA. In general the DES prepared with PA as HBD displayed the best solubility enhancements, being PA:U the best DES in terms of solubility enhancement (around 10-fold). Furthermore, the replacement of [Ch]Cl by U lead to an increase of 4-fold on the solubility of syringic acid, explained by the increase of dispersive interactions associated with U. Once again, no effects of the pH in the syringic acid solubility in DES aqueous solutions were perceived (see Figure 5).

Effect of DES molar ratio. The composition of DES (HBD:HBA ratio) plays an important role on its physico-chemical properties. By changing the HBD:HBA molar ratio it is possible to obtain a solid, a liquid or a combination of both at room temperature.^{42,43} It is thus important to understand if the solubility enhancement added by using DES resulted of a possible synergetic effect between

HBD and HBA. For this purpose, four carboxylic acids-based DES (PA:[Ch]Cl, LA:[Ch]Cl, GlyA:Pro and PA:U) with different molar ratio were studied in aqueous solutions with 25 wt % at 303.15 K. The detailed values of solubility and the respective standard deviations, are reported in Table S 3, at Supporting Information.

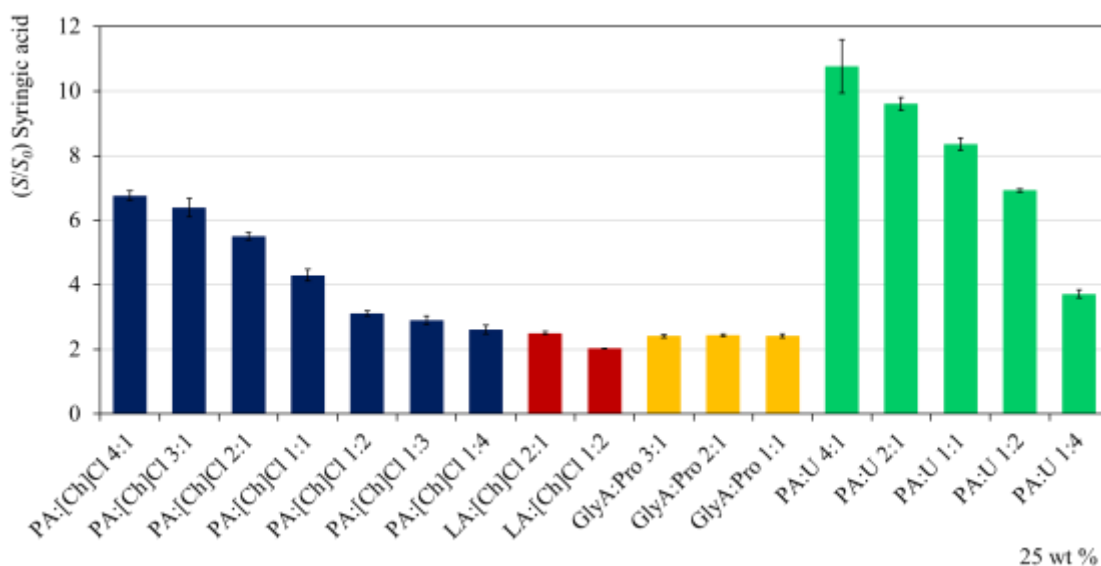


Figure 6. Influence of HBD:HBA molar ratio on the solubility enhancement of syringic acid in aqueous solutions with 25 wt % of DES, at 303.15 K.

According to the results shown in Figure 6 the molar ratio have a significant impact in the syringic acid solubility enhancement. Indeed, the solubility increased with the increase of HBD molar ratio, suggesting that the increase of dispersive interactions between the HBD and the syringic acid promotes the good performance of DES aqueous solutions. Again, better results can be obtained by using PA:U rather than PA:[Ch]Cl, what can be explained by the contribution of both components (HBD and HBA) to establish dispersive interactions with the lignin model compound.

The results here reported show the potential of PA:U aqueous solutions at 303.15 K to enhance the solubility of syringic acid. However, the focus of this work it is not the evaluation of the

performance of DES to solubilize syringic acid but the selection of the best DES to enhance the solubility of technical lignins. For a more complete evaluation of the DES potential, the solubility of other monomeric aromatics compounds such as syringaldehyde, vanillic and ferulic acids in aqueous solution with 25 wt % of PA:U at different molar ratio and 303.15 K were also studied and the results are reported in Figure 7. The detailed values of solubility and the respective standard deviations, are reported in Table S 3 and Table S 4, at Supporting Information.

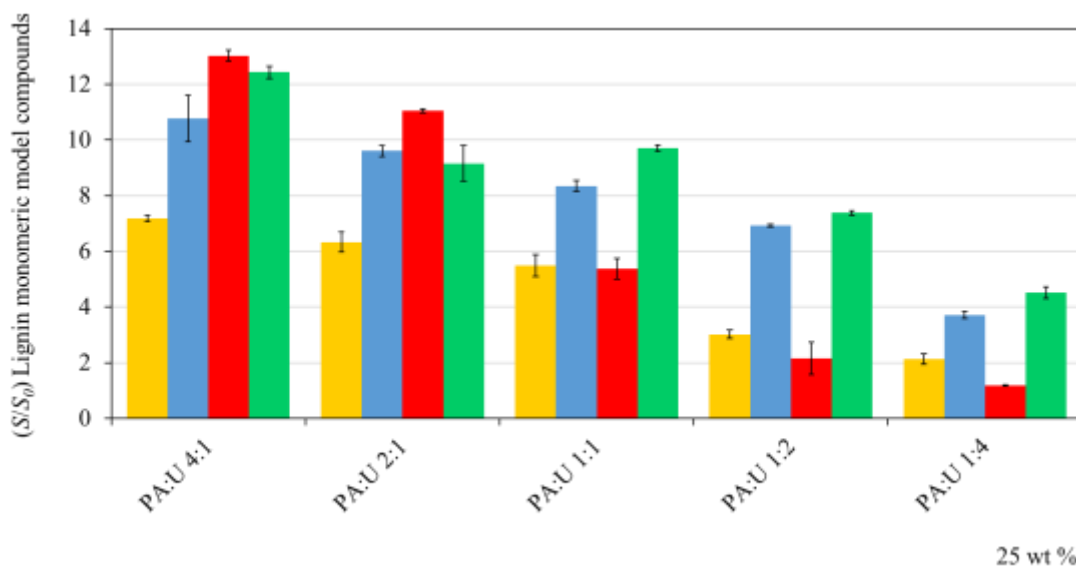


Figure 7. Influence of HBD:HBA molar ratio a on the solubility enhancement of lignin monomeric model compounds (syringaldehyde (green), syringic (blue), vanillic (yellow) and ferulic (red) acids), in aqueous solutions with 25 wt % of DES, at 303.15 K.

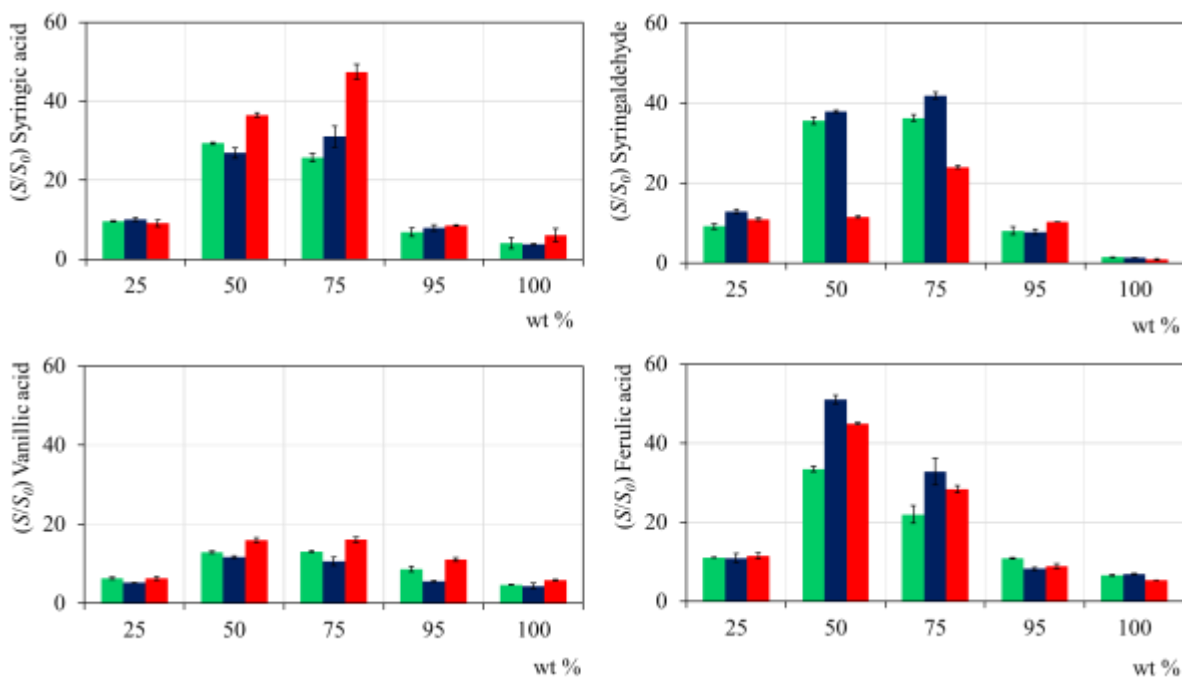
The results reported in Figure 7 show a clear impact of the HBD:HBA molar ratio on the solubility enhancement of all lignin monomeric model compounds investigated. The increase of molar ratio improve the lignin monomeric model compounds solubility, as shown previously in Figure 6 for syringic acid at the same conditions. Considering the solubility enhancement of each lignin monomeric model compounds in PA:U aqueous solutions, it is possible to observe that PA:U with molar ratio 4:1 and 2:1 show similar solubilities in the case of vanillic and syringic acids and

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3 a slight increase of solubility was observed for syringaldehyde and ferulic acid using PA:U 4:1.
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5 These results suggest that the enhanced solubilization observed in DES aqueous solutions resulted
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7 from a possible synergistic effect between HBD and HBA. Taking into account the similar
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9 solubility enhancement obtained for most of the lignin monomeric model compounds using PA:U
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11 4:1 and 2:1 aqueous solutions at 303.15 K, the PA:U 2:1 was selected to study the impact of the
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13 DES concentration and temperature upon its ability to enhance the solubility of the lignin
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15 monomeric model compounds investigated. The PA:U 2:1 has also the advantage over the PA:U
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17 4:1 of having a lower vapor pressure as result of a lower concentration in PA, and being closer to
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19 the eutectic point of the mixture thus having a larger liquidus range.
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24 **Effect of DES concentration and temperature.** The effect of DES concentration in aqueous
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26 solution was studied in the entire concentration range, from pure water to pure DES at three
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28 different temperatures (303.15, 313.15 and 323.15 K). The impact of PA:U 2:1 concentration and
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30 temperature on the solubility enhancement of lignin monomeric model compounds are presented
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32 in Figure 8. The detailed solubility values and the respective standard deviations, are reported in
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34 Table S 5, at Supporting Information.
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39 As expected, the solubilities of lignin monomeric model compounds in the studied
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41 concentrations range increase with the temperature. This trend may not be clear in Figure 8 due to
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43 the fact that the plot is represented in S/S_0 for each temperature, but it can be confirmed in the
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45 detailed data represented in Table S 5, at Supporting Information. Furthermore, it is clear the
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47 influence of PA:U 2:1 concentration on the solubility enhancement of each lignin monomeric
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49 model compound as depicted in Figure 8. Aqueous solutions of PA:U 2:1 at concentrations of 50
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51 and 75 wt % seem to allow the best solubility enhancement of lignin monomeric model
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53 compounds. Considering the combination of concentration and temperature effects, at 323.15 K
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3 and a concentration of 75 wt % the PA:U 2:1 enhanced the syringic and vanillic acids solubilities
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5 by 47 and 16-fold, respectively, while syringaldehyde achieved a 42-fold increase at 313.15 K and
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7 a DES concentration of 50 wt % at this temperature potentiated the solubility enhancement of
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9 ferulic acid of 51-fold at the same temperature. The shape of these curves, with strong maxima at
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11 intermediate compositions between pure water and the neat DES suggest that the solubility of these
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13 monomeric model compounds is being driven by a hydrotropic mechanism, previously described
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15 by us for the solubility of phenolic compounds in aqueous solutions of ionic liquids,⁴⁴ and
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17 confirmed by the presence of small aggregates typical from the density fluctuations²⁶ of the
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19 hydrotropic solubilization, using dynamic light scattering as described below. A hydrotropic
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21 solubilization driven by DES is here observed for the first time since, to the best of our knowledge,
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23 this has never been previously reported.
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52 **Figure 8.** Influence of PA:U 2:1 concentration and temperature on the solubility enhancement of lignin monomeric
53 model compounds (syringaldehyde, and syringic, vanillic and ferulic acids). The different temperatures studied were
54 303.15 K (green), 313.15 K (blue) and 323.15 K (red).
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3 The results hitherto reported reveal that PA:U 2:1 aqueous solutions, have an impressive potential
4 to solubilize lignin monomeric model compounds, specially ferulic acid and syringaldehyde at low
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6 temperature and syringic acid at high temperature. Its ability to solubilize vanillic acid seems to
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8 be weaker. The selectivity demonstrated here by PA:U 2:1 aqueous solution to solubilize aromatic
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10 aldehydes and acids, can open new pathways for the fractionation of phenolic compounds from
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12 complex mixtures obtained, for example, by lignin depolymerization e.g. from black liquors in
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14 pulp and paper industry, where the selective recovery and separation of these aromatic compounds
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16 is still an important goal in the biorefinery context aiming at their future valorization.⁴⁵ Finally,
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18 these results also suggest that aqueous solutions of PA:U 2:1 at 50 wt % could be good candidate
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20 to solubilize technical lignins. This subject will be investigated below.
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27 **Solubility of technical lignins.** Based on the results of lignin monomeric model compounds
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29 solubility in DES aqueous solutions reported above and keeping in mind the importance of
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31 dissolving lignin in aqueous media, the solubility of organosolv and kraft lignin using PA:U 2:1
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33 was evaluated in aqueous solutions with the DES concentrations of 25, 50, 75 and 100 wt % at
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35 two temperatures (313.15 and 323.15 K). The detailed values of solubility and the respective
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37 standard deviations, are reported in Table S 6, at Supporting Information. The solubility of
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39 technical lignins (organosolv and kraft) in pure water at 313.15 and 323.15 K and at atmospheric
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41 pressure were also measured aiming to determine the solubility enhancement added by using this
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43 DES. These values are reported in Table 4.
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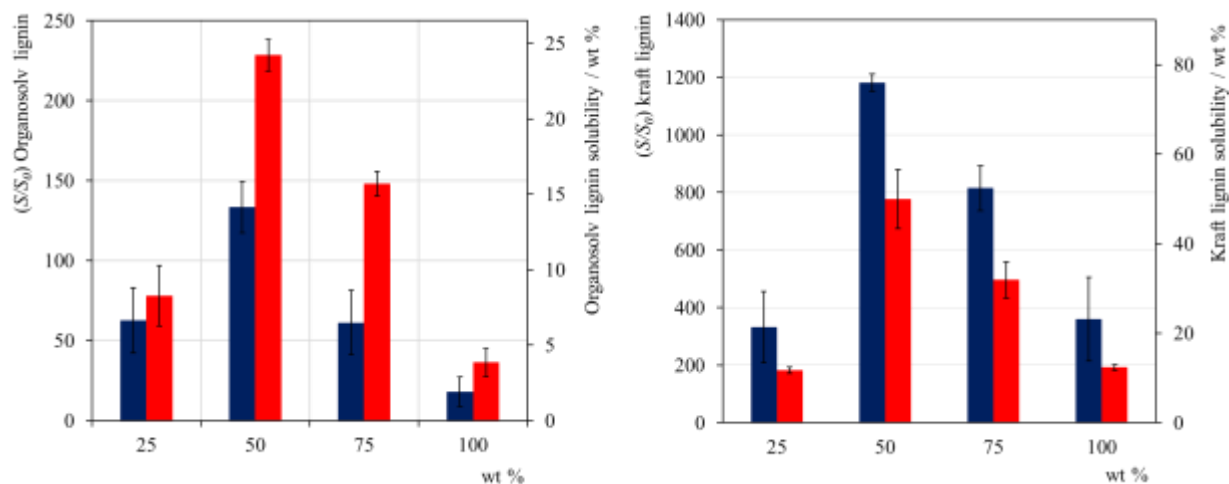


Figure 9. Influence of PA:U 2:1 concentrations on the solubility of organosolv and kraft lignin at 313.15 (blue) and 323.15 K (red).

The ability of DES (neat or in aqueous solutions) to enhance organosolv and kraft lignin solubility is depicted in Figure 9. The similarity of the solubility trend here reported with those previously observed for lignin model compounds under the same conditions is remarkable suggesting that the organosolv and kraft lignin solubilities in DES aqueous solutions are also driven by an hydrotropic mechanism, what is confirmed below by the presence of nanometric aggregates resulting from density fluctuations²⁶ typical of these solubilization mechanisms.⁴⁴ The organosolv and kraft lignin solubility enhancement depends on both the DES concentration and temperature, being the best results obtained at 313.15 and 323.15 K for kraft and organosolv lignin, respectively. Concerning the DES concentration, it is possible to observe that aqueous solutions at 50 wt % of PA:U 2:1 achieved an kraft lignin solubility enhancement of 1181.7 ± 29.2 fold and organosolv lignin solubility enhancement of 228.5 ± 9.7 fold. This is a remarkable performance of DES aqueous solution taking into account the low solubility of kraft and organosolv lignin in pure water reported in Table 4.

Considering the ability of alkali aqueous solutions (e.g. NaOH, pH 10) to solubilize lignin and aromatic and phenolic acids derived from lignin (e.g. vanillic, syringic acids) reported by

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3 Evstigneev,⁴⁶ some experiments were also carried out in order to compare the results here achieved
4 with the potential of NaOH aqueous solution (at pH 10) to enhance the solubility of kraft lignin
5 and lignin monomeric model compounds. The detailed values of solubility and the respective
6 standard deviations, are reported in Table S 7, at Supporting Information. Albeit aqueous NaOH
7 shows an effective solubility enhancement of about 16-fold in kraft lignins and 8-fold in lignin
8 monomeric model compounds, these values are much lower than those achieved with DES
9 aqueous solutions, further supporting their huge potential to solubilize technical lignins and lignin
10 monomeric model compounds.
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22 In this work, the evaluation of the DES potential to enhance the solubility of lignin was carried
23 out using a kraft lignin isolated from *E. globulus* industrial kraft liquor and organosolv lignin from
24 *E. globulus* wood (a more preserved lignin when compared with the kraft lignin). Taking into
25 account the chemical structure of the lignin it seems to be possible to anticipate the performance
26 of DES aqueous solution on the lignin solubilization through the evaluation of lignin monomeric
27 model compounds, as demonstrated in this work.
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36 **Dynamic light scattering.** In order to probe the mechanism of hydrotrophy, suggested above to
37 be driving the enhanced solubilization of the technical lignins and their monomeric precursors, the
38 presence of nanoaggregates, resulting from the density fluctuation²⁶ associated to the formation of
39 hydrotrope-solute aggregates, was assessed by dynamic light scattering (DLS) in aqueous
40 solutions (PA:U 2:1 50 wt % at 323.15 K) of technical lignins and lignin monomeric model
41 compounds . The size of the nanoaggregates detected in these solutions and the respective standard
42 deviations, are reported in Figure 10.
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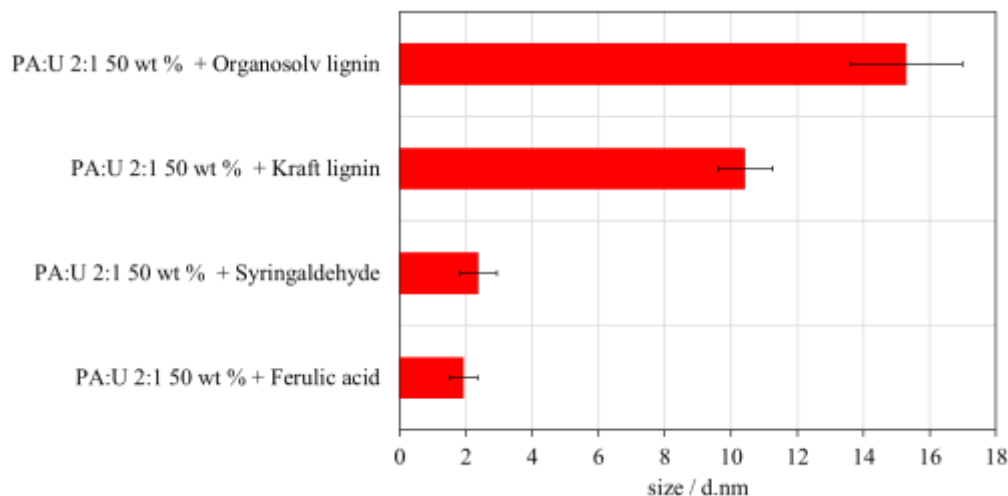


Figure 10. Nanoaggregate size present in saturated aqueous solutions of technical lignins and lignin monomeric model compounds in PA:U 2:1 at 50 wt % and 323.15 K, analyzed by DLS.

While no aggregates were observed in the aqueous solutions of PA:U 2:1 50 wt % the DLS results confirm the presence of nanoaggregates on the saturated aqueous solutions of technical lignins (kraft and organosolv) and lignin monomeric model compounds (syringaldehyde and ferulic acid) with sizes above 2 nm. These observations are in good agreement with the results previously reported by us for the solubility of phenolic compounds in aqueous solutions of ILs.⁴⁴ The presence of nanoaggregates in the solutions of syringic and vanillic acids were also probed by DLS, but the size of the aggregates observed were below the equipment resolution and thus cannot be trusted. The presence of these nanoaggregates is expected in hydrotropic solutions and supports the previous suggestion that the mechanism of hydrotropic solubilization of lignin and the aromatic and phenolic acids derived from lignin depolymerization is dominated by the hydrotrope-solute aggregation, as previously described for ionic liquids and other hydrotropes.^{26,44}

CONCLUSIONS

In this work, a comprehensive study on the solubility of lignin monomeric model compounds in neat DES and their aqueous solutions was performed. It was here disclosed, for the first time, the ability of DES to enhance the solubility of poorly soluble lignin derived compounds such as syringaldehyde, and syringic, vanillic and ferulic acids and organosolv lignin itself in aqueous solutions of DES through an hydrotropic mechanism, with the dispersive interactions being the main reason for the good performance of DES dissolution ability. The influence of HBDs and HBAs chemical structure, molar ratio, concentration and temperature on lignin monomeric model compounds solubility were investigated and the results show that both HBDs and HBAs play a significant role in the solubilization of these compounds with a possible synergistic effect between the two DES starting materials. Maximum solubilization of model compounds (ferulic, syringic and vanillic acids, and syringaldehyde) in PA:U 2:1 aqueous solution (51.1 ± 1.1 , 47.4 ± 1.9 and 16.1 ± 0.7 fold, and 41.9 ± 0.8 fold, respectively) were achieved at 50 or 75 wt % of PA:U 2:1 and 313.15 or 323.15 K.

Regarding the kraft and organosolv lignins solubilities in DES, a remarkably similar behavior to that obtained for lignin monomeric model compounds was observed. These results suggest that the lignin solubility in aqueous solution of DES results from a hydrotropic mechanism, confirmed by dynamic light scattering analysis and that it is possible to anticipate the lignin solubility in DES aqueous solution and select the best DES by studying the solubility of lignin monomeric model compounds. Maximum solubilization of kraft and organosolv lignins in PA:U 2:1 aqueous solution (1181.7 ± 29.2 and 228.5 ± 9.7 fold, respectively) were achieved at 50 wt % of PA:U 2:1.

This work provides a new understanding of lignin solubilization using DES aqueous solutions, and demonstrates the potential of DES to be used in new delignification and lignin conversion

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3 processes, as well as novel solvents to achieve the fractionation/purification of aromatic
4 components present in black liquor.
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9 ASSOCIATED CONTENT

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12 **Supporting Information.** The structural units of phenylpropane constituents of lignin; the
13 calibration curves of lignin monomeric model compounds and alkali lignin in water at 298.15 K;
14 the calibration curve of alkali, kraft and organosolv lignin in two different DES (EG:[Ch]Cl 2:1
15 and EG:[N₄₄₄₄]Cl 2:1) at 353.15 K; the regression analysis of respective calibration curves; the
16 experimental solubilities of lignin monomeric model compounds in 25 wt % aqueous solutions of
17 DES at 303.15 K; the experimental solubilities of lignin monomeric model compounds in PA:U
18 2:1 aqueous solutions at three different temperatures; the experimental solubilities of organosolv
19 and kraft lignin in PA:U 2:1 aqueous solutions at two different temperatures; and the experimental
20 solubilities of kraft lignins and lignin monomeric model compounds in aqueous NaOH solutions
21 with pH 10 at different temperatures These materials are available free of charge on the ACS
22 Publications website at <http://pubs.acs.org>.
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48 **Author Contributions**

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51 The manuscript was written through contributions of all authors. All authors have given approval
52 to the final version of the manuscript.
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57 **Notes**
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3 The authors declare no competing financial interest.
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7 ACKNOWLEDGMENTS. This work was developed in the scope of the project CICECO-Aveiro
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9 Institute of Materials (Ref. FCT UID /CTM /50011/2013), financed by national funds through the
10
11 FCT/MEC and when applicable co-financed by FEDER under the PT2020 Partnership Agreement.
12
13 FCT is acknowledged for funding the project DeepBiorefinery (PTDC/AGR-TEC/1191/2014).
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15 The authors wish to thank FCT and the Navigator Company, for the awarding of a Ph.D. grant
16
17 (SFRH/BDE/103257/2014) to Belinda Soares. Carmen S. R. Freire acknowledges FCT/MCTES
18
19 for a research contract under the Program “Investigador FCT 2012”. The Navigator Company was
20
21 gratefully acknowledged for supplying *Eucalyptus globulus* wood and technical lignin samples.
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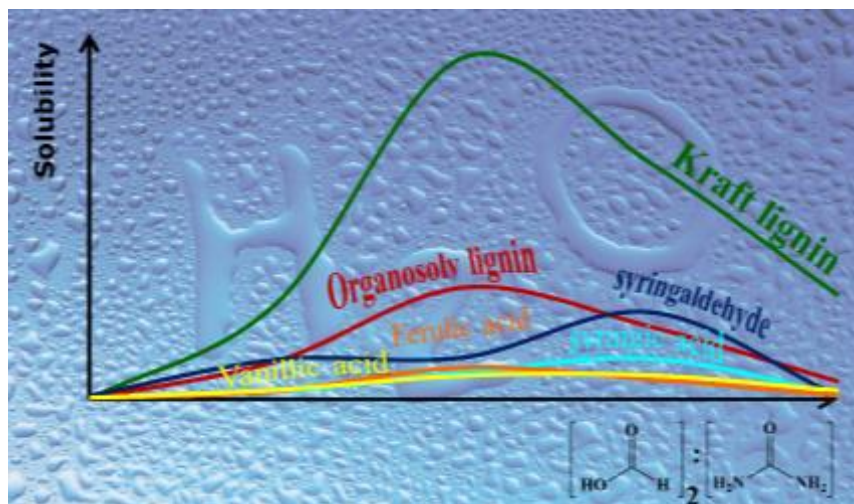
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Table of contents (TOC) graphic.



Manuscript title: Enhanced solubility of lignin monomeric model compounds and technical lignins in aqueous solutions of deep eutectic solvents

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Synopsis. Aqueous solutions of DES enhance the solubility of technical lignins more than 200 times opening the possibility for new lignin extraction and conversion processes.