

An investigation of Kraft lignin solubility in Protic Ionic Liquids and their aqueous solutions

Rafael Macedo Dias, Livia Chagas Gomes Petrin, Filipe Hobi Bordon Sosa, André Miguel da Costa Lopes, Joao A.P. Coutinho, and Mariana Conceição Costa

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6 **1 An investigation of Kraft lignin solubility in Protic Ionic**

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9 **2 Liquids and their aqueous solutions**

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14 **3** Rafael M. Dias^a, Lívia C. G. Petrin^a, Filipe H. B, Sosa^{a,b}, André M. da Costa

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17 **4** Lopes^b, João A. P. Coutinho^b, Mariana Conceição Costa^{a,*}.

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20
21 **5** *^aDepartment of Process and Product Design (DDPP) - School of Chemical Engineering*

22 *(FEQ), University of Campinas (UNICAMP), Av. Albert Einstein, 500, Campinas, São*

23 *Paulo, 13083-852, Brazil.*

24 **6** *^bCICECO, Aveiro Institute of Materials, Department of Chemistry, University of Aveiro,*

25 *3810-193 Aveiro, Portugal.*

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35 **11** *Corresponding author: mcdcosta@unicamp.br

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3 **1 ABSTRACT**
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6 **2** In this study, the potential of alkanolammonium-based Protic Ionic Liquids (PILs)
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9 **3** aqueous solutions as solvents of Kraft lignin was evaluated. The results showed that the
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12 **4** PILs' anion has a key role in lignin dissolution, while the cation plays a secondary role.
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15 **5** The presence of extra hydroxyl groups in the anion structure negatively affects the lignin
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18 **6** solubility, while the increase of the cation alkyl chain favors this process. Using
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21 **7** mechanical agitation all tested PILs required 8 h to reach saturation, excepting for
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24 **8** lactate-based PILs (at least 24 h). The efficiency of lignin dissolution was improved with
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28 **9** ultrasounds achieving saturation in less than 4 hours. Finally, the recyclability of two PILs
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31 **10** was herein demonstrated for at least 3 cycles. The tris(2-hydroxyethyl)ammonium lactate
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34 **11** (THEAL) presented the best ability to dissolve Kraft lignin (> 47 wt%) among the tested
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38 **12** PILs. This result shows the capacity of PILs as excellent media to dissolve lignin.
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1. Introduction

The dependency on non-renewable resources is a current societal issue that must be addressed. In this scenario, the use of biomass as raw material has been attracting the interest of scientific community as one of the most promising renewable sources of carbon and it can be a solution to replace the excessive use of non-renewable feedstocks. The conversion of biomass into energy, fuels, materials and high-value products through a series of integrated and sustainable processes in the framework of the biorefinery concept has been pursued by the academic and industrial communities.

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Among different types of biomass, lignocellulosic materials are the most abundant and available in the world and their valorization has been tentatively performed.⁵ Cellulose, hemicellulose and lignin are the major components of lignocellulose, but they are strongly linked into a recalcitrant matrix difficult to disrupt.^{6,7} Cellulose and hemicellulose are polysaccharides attached through hydrogen bonds and van der Waals interactions, possessing a structural role in the plants.^{8,9} Lignin is defined an amorphous material, and consists of phenylpropanoid units linked by carbon-carbon and ether bonds forming a complex three-dimensional polymer, whose function is to provide resistance against

1 pathogens, rigidity to the plant cell wall and compressive strength to the fibers and plant
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7 2 tissues.¹⁰
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11 3 The singular structure and physicochemical properties of lignin have a significant
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14 4 potential for the production of several types of aromatic materials and compounds as
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17 5 alternative to petrochemical-based products.¹¹⁻¹⁵ Despite the fact that lignin can be
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20 6 converted into fine chemicals, the technology to convert it still needs to be developed.¹⁶
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23 7 According to the International Lignin Institute, annually between 40-50 million tons of
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26 8 lignin are produced, mostly as non-commercial waste product.¹⁷ Only 2 % of this amount
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29 9 is commercialized as low-value products (e.g. dispersing or binding agents), while the
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33 10 rest is burned as fuel.^{11,18} Therefore, more efforts must be pursued to achieve a
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36 11 sustainable lignin valorization and to meet a biobased economy. In this regard, the
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39 12 evaluation of an appropriate solvent for lignin would facilitate the development of efficient
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43 13 processes for its conversion.
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46 14 Over the years, studies have been reported the solubility of kraft lignin in organic
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49 15 solvents.¹⁹⁻²² In general, alcohol, ester and organochloride compounds such as
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53 16 methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, ethyl acetate, ethylene carbonate,
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56 17 propylene carbonate, chloroform and dichloromethane are considered poor solvents for
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59 18 lignin dissolution when applied at low temperatures (from 293.15 to 323.15 K).^{19,22,23} Low
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1 lignin solubility values (< 1 wt%) were reported by using 1,4-dioxane, acetone, water,
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7 2 diethyl ether and tetrahydrofuran as solvent in an experiment developed at 296.15 K
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10 3 under ultrasound agitation during 10 minutes.¹⁹ Some organic acids and alcohol
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13 4 compounds such as formic acid, glycerol and ethylene glycol showed higher dissolution
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16 5 performance, and were capable of dissolving around 20, 25, and 31 wt% of lignin,
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19 6 respectively, at 293.15 K by using mechanical agitation.^{20,23} A remarkable achievement
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22 7 for solubility of kraft lignin was reported by Achinivu (2014), in which the use of pyridine
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25 8 and 1-methylimidazole at 363.15 K and 24 hours of agitation has increased the solubility
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28 9 to value greater than 50 wt%.²⁴ Moreover, Xue et al. (2016) tested binary mixtures of γ -
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32 10 valerolactone with different organic solvents.²¹ The authors demonstrated that γ -
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35 11 valerolactone aqueous solutions were capable of dissolving more than 35 wt% of kraft
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38 12 lignin at 70 °C and 2 hours of agitation, while dimethyl sulfoxide was capable of dissolving
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41 13 17 wt% of kraft lignin under the same experimental conditions.²¹ Although good results
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44 14 with organic solvents have been achieved, alternative solvents have been tested to
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47 15 achieve even higher lignin solubility values. Among these alternative solvents, Ionic
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51 16 Liquids (ILs) emerged as a promising class of solvents to promote lignin dissolution and
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54 17 its extraction from lignocellulosic biomass.^{20,25-32} They have been considered as a more
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1 sustainable and efficient alternative to traditional organic solvents, which are usually
2 hazardous and present low selectivity for lignin dissolution.³³

3 By definition, ILs are salts with melting points lower than 100 °C, and are composed of cations
4 and anions.^{34,35} They present low vapor pressure, high conductivity, thermal and chemical
5 stability, making them useful in many fields such as synthesis and catalysis, biotechnology,
6 pharmaceuticals and medicine, electrochemistry, extraction and separation, among others.^{36–38}
7 Protic Ionic Liquids (PILs) are, in particular, a class of ILs that has witnessed a growing the
8 interest from the scientific community lately. These ILs are easily synthesized by a proton transfer
9 from an organic acid to an organic base, which is a considerably cheap and easier synthesis
10 procedure than that of traditional aprotic ILs.³⁹ Due to this advantage, and also to their remarkable
11 properties, such as high proton conductivity, chemical and thermal stability, PILs have been
12 extensively studied.^{39–45}

13 Recently, PILs have been proposed for lignin dissolution.^{20,28} The ability of 18 novel
14 multiaromatic PILs for Kraft lignin dissolution was visually demonstrated by Merino et al.
15 (2018) using microwave-assisted irradiation at 363.15 K. The results showed that 42 wt%
16 lignin can be dissolved in 2, 3, 4, 5-Tetraphenyl-1*H*-imidazolium methanesulfonate
17 ([TPIM][MeSO₃]) at 363.15 K in few minutes.²⁸ The lignin solubility was also determined
18 in pyridinium based PILs aqueous solutions by Rashid et al. (2016). The pyridinium
19 formate ([Py][For]) was the best PIL, achieving 70 wt% lignin solubility at low temperature
20 (348.15 K) within 1 hour.²⁰ More recently, Dias et al. (2020) demonstrated the ability of
21 seven alkanolammonium based PILs composed of monocarboxylic anions to dissolve

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3 1 Kraft lignin, achieving more than 38 wt% solubility at 353.15 K when using 2-
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6 2 hydroxyethylammonium propionate ([HEAP]). The authors also reported, in general, a
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10 3 negative effect of water on lignin solubility, however, a hydrotropic behavior was
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13 4 observed for 2-hydroxyethylammonium octanoate (HEAO) that enhanced the lignin
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16 5 solubility in aqueous solutions to a maximum value at 40 wt% water content.⁴⁶
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20 6 A wide range of cation and anion combinations could be used to synthesize PILs, but
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23 7 only a few of these possibilities were reported in literature for lignin dissolution.
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26 8 Therefore, new combinations of cations and anions were tested in this study and the role
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30 9 of each ion in the solubility of lignin was investigated as a continuation of the work
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33 10 published elsewhere.⁴⁶ PILs aqueous solutions composed of alkanolammonium cations
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36 11 with malate, malonate, succinate, glycolate and lactate anions were studied for their
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39 12 ability to dissolve Kraft lignin. The lignin solubility in those systems was correlated to their
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42 13 chemical structure. Moreover, the time-dependence of lignin dissolution in PILs was
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45 14 evaluated as another parameter to address their efficiency.

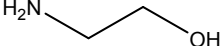
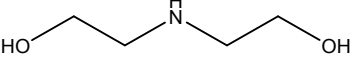
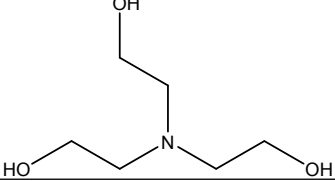
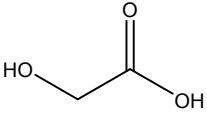
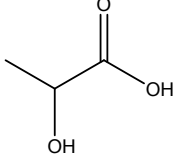
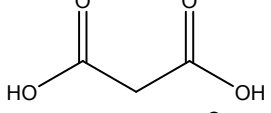
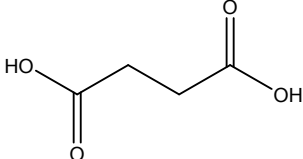
15 2. Experimental

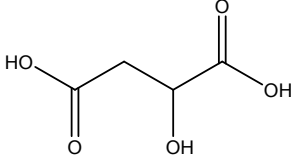
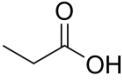
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3 2.1 Chemicals
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5 The acid and base precursors used to synthesize the PILs studied in this work are
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9 depicted in Table 1. All reagents were used as received. *Eucalyptus globulus* isolated
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19 lignin from Kraft process was supplied by Suzano Papel & Celulose – Brazil.

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5 **Table 1.** Purities, chemical structures and suppliers of the pure bases and acids used in
6 this study

| Chemical Name | Chemical Structure | Purity (%) | pKa ^a | Supplier |
|----------------------------------|---|------------|------------------|--------------------------|
| Bases | | | | |
| 2-hydroxyethylamine (HEA) |  | ≥ 98 | 9.50 | Sigma Aldrich |
| bis(2-hydroxyethyl)amine (BHEA) |  | ≥ 98 | 8.96 | Sigma Aldrich |
| tris(2-hydroxyethyl)amine (THEA) |  | ≥ 98 | 7.76 | Sigma Aldrich |
| Acids | | | | |
| Glycolic acid (G) |  | 70 | 3.83 | Dinâmica |
| Lactic acid (L) |  | 85 | 3.86 | Sigma Aldrich |
| Malonic acid (Mn) |  | 99 | 2.85/ 5.70 | ReagentPlus [®] |
| Succinic acid (Su) |  | 99 | 4.21/ 5.64 | Synth |

| | | | | |
|-----------------------|---|------|---------------|-------------------|
| Malic acid (M) |  | 99 | 3.51/ 5.03 | Dinâmica |
| Propionic acid (P) |  | ≥99% | 4.88 | Acros organics |

^a PubChem database. (PubChem, 2020)

2.2 Synthesis of PILs and their characterization

The following 7 PILs were synthesized in an acid-base reaction as described in the next paragraph and previously reported by Álvarez et al. ⁴⁸ and by Dias et al. ^{46,49}: 2-hydroxyethylammonium malonate (HEAMn), 2-hydroxyethylammonium malate (HEAM), 2-hydroxyethylammonium succinate (HEASu), 2-hydroxyethylammonium glycolate (HEAG), 2-hydroxyethylammonium lactate (HEAL), bis(2-hydroxyethyl)ammonium lactate (BHEAL), and tris(2-hydroxyethyl)ammonium lactate (THEAL). The reagents were weighed in stoichiometric proportions. The base was placed in a bottom flask and stirred with a magnetic bar, while an aqueous solution of acid was prepared and added dropwise to the base. An ice bath was used to control the reaction temperature. The final solution was maintained under stirring for 24 hours. The IL solution was then placed in a rotary evaporator to remove any excess of water or reagents. The water content was determined using a Metrohm 831 Karl Fischer coulometer and these values were considered in the preparation of PIL aqueous solutions. The PILs were characterized through ¹H NMR, ¹³C NMR and FT-IR (Electronic Supporting Information – ESI).

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3 1 For the FT-IR analysis, a PerkinElmer spectrometer (Spectrum BX) equipped with a
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6 2 single horizontal Golden Gate ATR cell (attenuated total reflectance) and diamond
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9 3 crystal was used. All spectra were acquired with 32 scans at 4 cm⁻¹ of resolution and a
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12 4 wavenumber range between 4000 cm⁻¹ and 600 cm⁻¹ (Figures S1-S7 in ESI).

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17 5 For NMR analysis, IL samples were dissolved in deuterated DMSO (DMSO-d₆) as
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20 6 solvent and tetramethylsilane (TMS) as an internal reference. All spectra were recorded
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23 7 by a Bruker AVANCE 300 NMR at 300 MHz (Figures S8-S21 in ESI).

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31 9 *2.3 Kraft lignin solubility in PILs aqueous solutions under conventional heating*

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33 10 Excess of Kraft lignin was added to 2.0 ± 0.05 g of each PILs aqueous solutions (5, 15,
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36 11 25, 40, 50, 60, 75, 80, 85, 87.5, 90, 92.5 and 95 wt% of PIL) or pure water in glass vials.

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39 12 The vials were sealed and placed on a specific aluminum disk support, which was
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42 13 transferred to a stirring plate with heat control Pt1000 (H03D Series from LBX
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45 14 Instruments). The aluminum disk support was maintained at constant temperature
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48 15 (313.15, 323.15, 333.15 or 353.15 K) and the samples were kept under constant
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51 16 agitation (200 rpm - provided by magnetic bar stir) until saturation. The influence of time
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54 17 on the Kraft lignin solubility was also evaluated and the same methodology was
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57 18 performed at different periods of time (1, 2, 4, 8, 16, 24 and 48 hours). The solid phase
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3 1 was then separated from the liquid phase using PTFE filters (0.45 μm pore size). The
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6 2 filtered liquid samples were diluted using dimethylsulfoxide (DMSO) and the dissolved
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9 3 lignin was quantified by UV-spectroscopy (SHIMADZU UV-1700, Pharma-Spec
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12 4 spectrometer) at 280 nm wavelength. The lignin concentration was determined by
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15 5 appropriate calibration curves (Table S1 in ESI). All experiments were made at least in
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18 6 duplicate and the results were expressed as means.
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28 8 *2.4 Kraft lignin solubility in PILs aqueous solutions using ultrasonic heating water bath*
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30 9 The Kraft lignin dissolution in some neat PILs was also evaluated using ultrasound
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33 10 (Model 1400 A, Unique, Brazil). The ultrasonic water bath was rated at
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36 11 135 W with a resonating frequency of 40 kHz, while water was recirculated ensuring
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39 12 constant temperature during the assays. The temperature was monitored with a
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42 13 thermometer (PT-100 temperature sensor (± 0.1 K)) and the experiments were
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45 14 performed with satisfactory temperature control (± 0.5 K). The sample preparation and
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48 15 the determination of lignin solubility in PILs were performed as described in section 2.3.
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3 1 2.5 *Measurement of PILs viscosity*
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5 2 The viscosities of PILs (5 wt%) at different temperatures (303.15 to 333.15 K) were
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8 3 measured using an automated micro viscosimeter (Anton Paar, AMVn, Germany),
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11 4 applying the falling ball method. The water content was determined (Metrohm 831 Karl
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15 5 Fischer coulometer) before each measurement. During the viscosimeter operation the
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18 6 temperature was kept constant within ± 0.01 K.
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26 8 2.6 *PILs recyclability*
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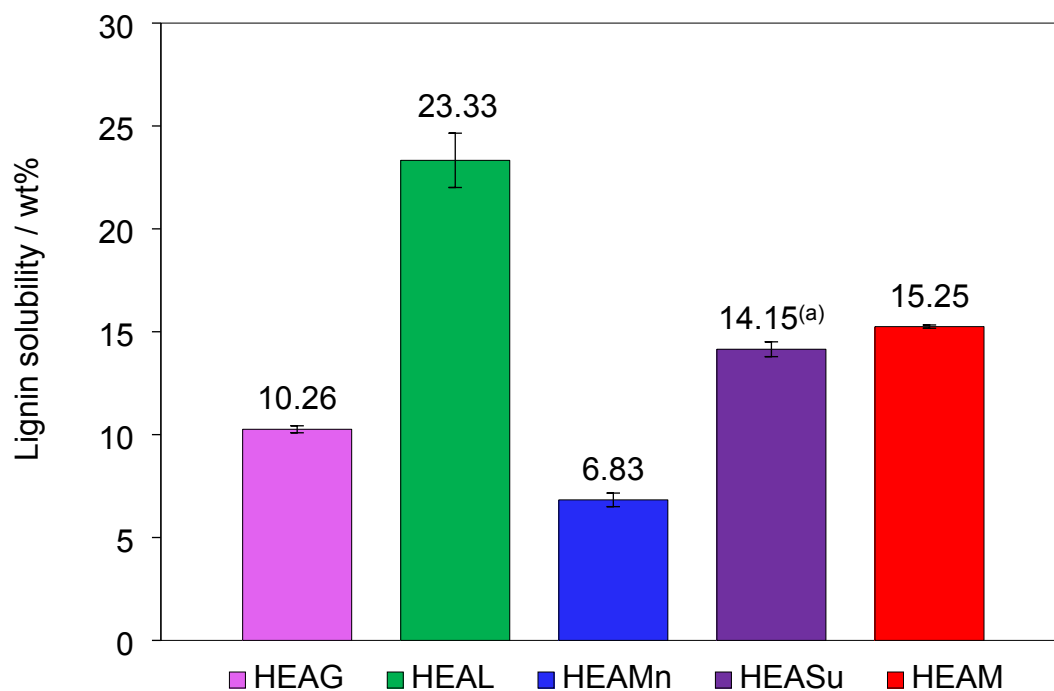
28 9 Deionised water was added to the mixture of HEAM and THEAL aqueous solution
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31 10 saturated with lignin to promote lignin precipitation. An ice bath (278.15 K) was used to
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35 11 decrease the temperature of the solution favouring the precipitation process. The
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38 12 precipitated lignin was separated by vacuum filtration, washed with water and the
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41 13 resulting PIL aqueous solution was subjected to rotary vacuum evaporation process
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44 14 (333.15 K and 10 kPa for 2.0 hours) until a 5 wt% water content was achieved. The
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47 15 recovered HEAM and recovered THEAL aqueous solutions were reused in lignin
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51 16 solubility assays as described in Section 2.3. The lignin that remained dissolved in PIL
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54 17 solution after each cycle was determined using the same experimental procedure (UV
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57 18 method) described in section 2.3. The PIL sample containing the lignin dissolved was
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3 1 diluted using dimethylsulfoxide (DMSO) and the lignin was quantified by UV-
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6 2 spectroscopy at 280 nm wavelength. The lignin concentration was determined by
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9 3 appropriate calibration curves (Table S1 in ESI).
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18 5 **3. Results and discussion**

21 6 *3.1 The effect of anion structure on Kraft lignin solubility*

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24 7 The chemical nature of the anion of aprotic ionic liquids (AILs) has been shown to play
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27 8 a major role on the lignin solubility.^{27,50,51} To evaluate this effect on PILs, 2-
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30 9 hydroxyethylammonium-based PILs composed of mono and dicarboxylic anions with
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33 10 different carbon chain lengths (C2 to C4), with or without α -hydroxyl groups, were tested
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37 11 for Kraft lignin solubility at 323.15 K. The solubility values measured are presented in
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40 12 Figure 1 and Table S2 (along with the corresponding standard deviations) in ESI.
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2 **Figure 1.** Kraft lignin solubility (wt%) at 323.15 K in neat PILs with 5 wt% water content except
3 for HEASu. ^(a) The lignin solubility in HEASu was determined in aqueous solution containing 20
4 wt% of water content, since at lower water contents it remains as solid at
5 323.15 K.

6

7 The results reported in Figure 1 show that the structure of the anion, and its chemical
8 properties, have a significant impact on the Kraft lignin solubility in PILs. Amongst the
9 studied solvents, HEAL showed the best performance for lignin solubility reaching a
10 value of 23.33 wt%, which was more than 2-fold the solubility value obtained with HEAG
11 (10.26 wt%). However, the Kraft lignin solubility in HEAL is lower than in neat 2-
12 hydroxyethylammonium propionate (HEAP) reported elsewhere at the same
13 temperature (> 30 wt%). ⁴⁶ With regard to dicarboxylic-based PILs, HEAM achieved

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3 1 15.25 wt% lignin solubility, while HEAMn presented the lowest solubility (6.83 wt%) of all
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6 2 the compounds studied. Exceptionally, HEASu mixtures containing more than 80 wt%
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9 3 PIL were solid at 323.15 K, thus lignin solubility at these conditions were not determined.
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13 4 Nevertheless, 14.15 wt% lignin solubility was determined as the best result for HEASu
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16 5 with 80 wt% PIL content.

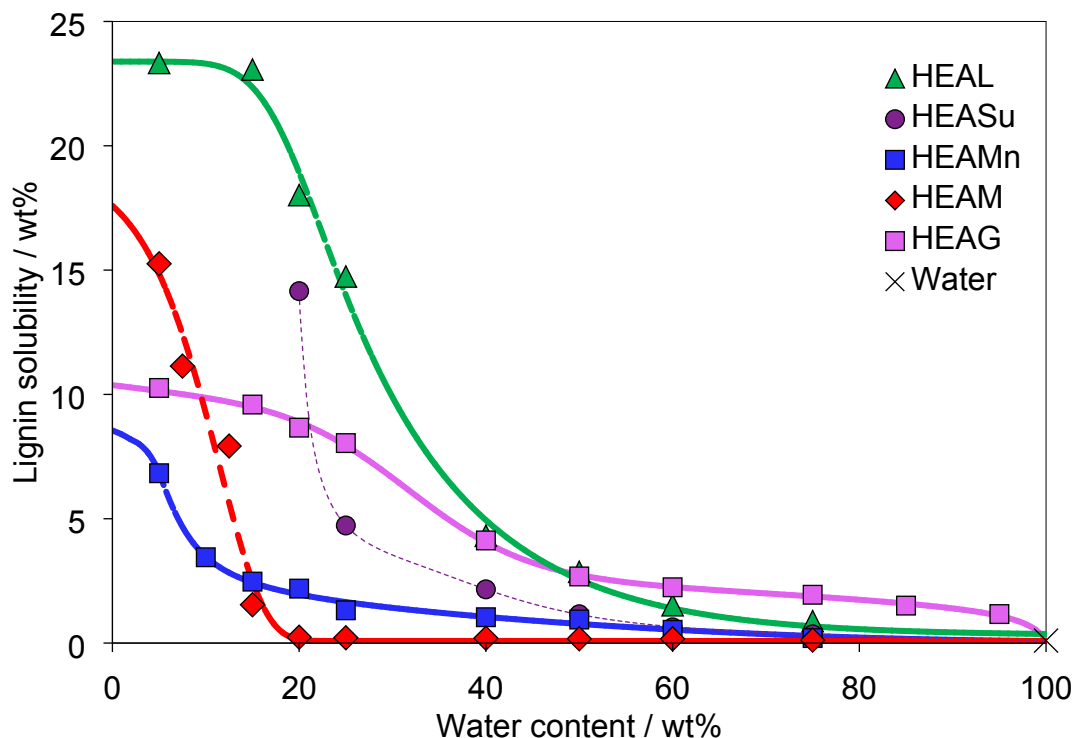
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20 6 Therefore, the performance of examined PILs (with 5 wt% water content) for Kraft lignin
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23 7 solubility can be ordered as follows: HEAL > HEAM > HEAG > HEAMn. These results
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26 8 show that increasing the carbon chain length of the anion from C2 to C3, particularly
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29 9 from glycolate to lactate, a better lignin solubility is obtained. For dicarboxylic anions, the
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33 10 increase of carbon chain length of the anion from C3 (malonate) to C4 (succinate and
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36 11 malate) favored lignin solubility. These results suggest that the dispersive interactions
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39 12 between alkyl carbon chain and lignin molecules contribute significantly to increase the
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43 13 solubility of lignin.⁵²

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46 14 In literature, the correlation between the lignin solubility and the alkyl chain length of the
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49 15 anion has been previously investigated by several authors.^{29,46,53} Hou et al. (2015)
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53 16 demonstrated that lignin solubility was favored by increasing the carbon chain length of
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56 17 the alkanoate anions using different cholinium-based ILs. Recently, Dias et al. (2020)
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59 18 also observed this behavior and showed that the larger the alkyl chain length of the

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3 1 carboxylate anions (at least up to a six-carbon chain length) in monoethanolammonium-
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6 2 based PILs, the higher is the solubility of lignin in these solvents which is related to a
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9 3 better affinity between lignin and the PILs. ⁴⁶ According to Xu et al. (2017) the alkyl chain
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12 4 in the anion structure is able to interact with lignin. ²⁹ The authors performed ¹³C NMR
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15 5 and ¹⁵N NMR measurements to achieve a better understanding on the lignin dissolution
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18 6 mechanism and to support their results. Initially, Xu et al. (2017) dissolved lignin in ILs
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21 7 aqueous solutions, and checked the NMR signals. They observed that the signal of COO⁻
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24 8 groups remained constant compared with ILs aqueous solutions without lignin, while the
25
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27 9 chemical shifts of alkyl carbon chain decreased. These observations suggested that
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29
30 10 there were interactions between the alkyl carbon chain in the anion and the lignin, leading
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33 11 to an increase of the electron cloud density in the alkyl chain anionic part. Therefore,
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36 12 increasing the alkyl chain of the anion may favor the lignin dissolution in PILs, since more
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39 13 interactions between lignin and the anion are allowed. This is confirmed when the
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42 14 abilities for lignin dissolution between HEASu and HEAMn or between HEAL and HEAG
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45 15 are compared. The longer alkyl chain is also the reason why succinate and lactate-based
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48 16 PILs exhibit higher lignin solubility than their counterparts.
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55 17 The solubility of Kraft lignin in 2-hydroxyethylammonium acetate (HEAA) and 2-
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58 18 hydroxyethylammonium propionate (HEAP) at 323.15 K was determined in a previous
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3 1 study.⁴⁶ When comparing such results with those obtained in this work, *i.e.*, between
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6 2 HEAA (22.12 wt%)⁴⁶ and HEAG (10.26 wt%) as well as between HEAP (30.86 wt%)⁴⁶
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9 3 and HEAL (23.33 wt%), it is clear that the presence of an α -hydroxyl group in the anionic
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12 4 structure decreases the ability of these solvents to dissolve lignin. This extra hydroxyl
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15 5 group present in both HEAG and HEAL increases the polarity of the anion and induces
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18 6 the formation of hydrogen bonds between the PIL anions, reducing their interaction with
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22 7 lignin. This behavior was previously reported using deep eutectic solvents to dissolve
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25 8 lignin monomeric model compounds by Soares et al. (2017) and toluene by Wang et al.
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28 9 (2016).^{52,54}
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33 10 The effect of water on lignin solubility in PILs was also evaluated in this study. The lignin
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36 11 solubility values as function of water content (Figure 2 and Table S2 in ESI) revealed an
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39 12 abrupt decrease of lignin solubility in most PILs when adding water. For instance, the
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42 13 Kraft lignin solubility in HEAM aqueous solutions was the most affected, with a decrease
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45 14 from 15.25 wt% to just 1.54 wt% lignin solubility observed as the water content increases
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48 15 from 5 to 15 wt%. This behavior was less pronounced for HEAMn and HEAL at the same
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51 16 water content, but still a substantial decrease of lignin solubility was observed in these
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54 17 systems, which shows the anti-solvent character of water for lignin. On the other hand,
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57 18 the less negative effect of water on lignin solubility by declining from 10.26 to 9.59 wt%
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1 was observed for HEAG. In order to confirm the anti-solvent role of water, a negligible
2 value of lignin solubility on pure water (0.10 wt%) was measured at 323.15 K.



3
4 **Figure 2.** Kraft lignin solubility in HEAL, HEASu, HEAMn, HEAM, and HEAG aqueous
5 solutions and pure water at 323.15 K. Lines are guide for eyes.

6
7 Some authors have previously reported the negative effect of water on the Kraft lignin solubility
8 in PILs.^{20,29,51} The anti-solvent character of water for lignin explains the lower lignin solubilities
9 in PILs aqueous solutions, the interaction between water and PILs seems to play a role. Xu et al.
10 (2017) mentioned that the solvation by water molecules of the cation and anion of the IL impairs
11 the interactions between IL and lignin.²⁹ To reinforce this argument Ji et al. (2012) investigated
12 the interactions between water–IL–lignin by applying theoretical calculations and concluded that
13 the interaction energy and the active sites of IL and lignin decrease with the addition of water,
14 making the bonds between them weaker or even destroyed.⁵⁵ The data here obtained shows,
15 however, that the water impact on lignin solubility depends on the PIL anionic structure. The

1 negative influence of water on lignin solubility in PILs seems to be more pronounced for anions
 2 with a higher number of hydrogen bonding accepting sites, like malate (Table 2). This suggests
 3 that water molecules strongly crowd the hydrogen bond accepting sites (carboxylate and hydroxyl
 4 groups) and prevent these anions to establish interactions with lignin. On the opposite, the
 5 glycolate anion that possesses only one carboxylate group is less sensitive to water interaction,
 6 thus leading to a lower decline in lignin solubility as observed (Table 2). Therefore, anions with
 7 a higher hydrophilicity favor the interactions between water molecules and PIL, decreasing the
 8 lignin solubility. Similar results were observed with different choline carboxylate ILs (using
 9 mono, di, and tricarboxylate anions) in Kraft lignin dissolution.²⁹

10 **Table 2.** The influence of the number of carboxylate and hydroxyl groups and total hydrogen
 11 bond accepting (HBA) sites in PILs anions on the variation of lignin solubility between 5 and 25
 12 wt% water content in corresponding PILs.

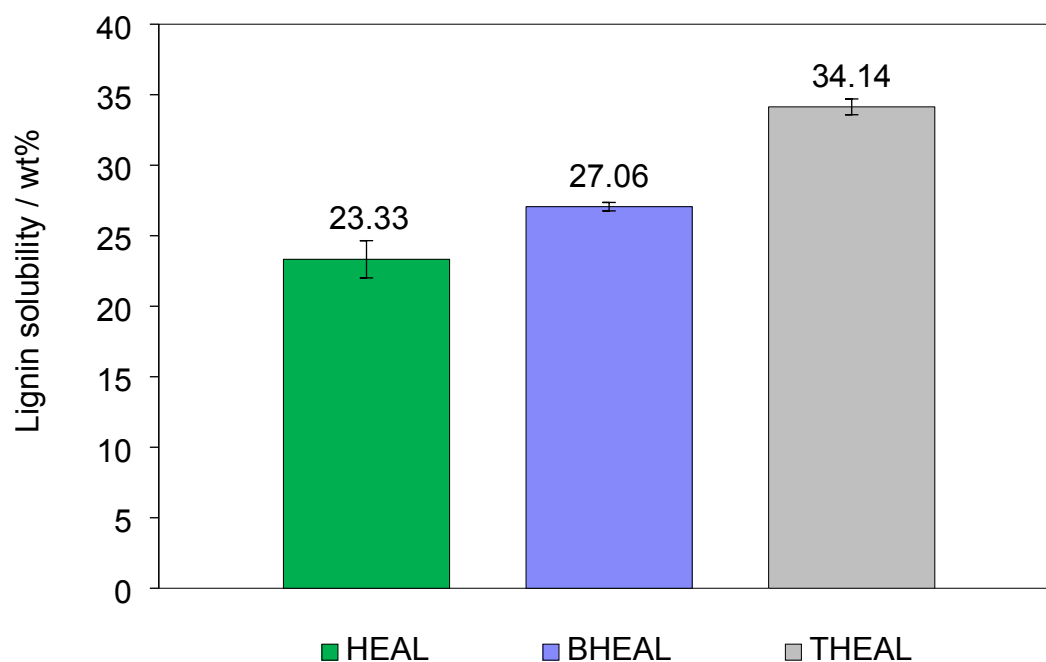
| Anion | COO-/COOH | OH | Total HBA sites ^(a) | $\Delta\%$ lignin solubility decline ^(b) |
|----------------|-----------|----|--------------------------------|---|
| Glycolate (C2) | 1 | 1 | 3 | -21.6 |
| Lactate (C3) | 1 | 1 | 3 | -36.8 |
| Malonate (C3) | 2 | 0 | 4 | -80.7 |
| Succinate (C4) | 2 | 0 | 4 | -66.6 ^(c) |
| Malate (C4) | 2 | 1 | 5 | -98.6 |

13 ^(a) COO-/COOH = 2 HBA sites and OH = 1 HBA site; ^(b) variation of lignin solubility by taking
 14 into account the difference between lignin solubilities obtained with PILs at 5 and 25 wt% water
 15 content; ^(c) an exception was made for HEASu, in which the difference between lignin solubilities
 16 with HEASu at 20 and 25 wt% water content was considered for the reasons mentioned before.

18 3.2 The effect of cation structure on Kraft lignin solubility

19 In order to investigate the influence of the PIL cation on the Kraft lignin solubility, lactate was
 20 chosen as the anion counterpart, since it revealed the best performance among the tested anions.
 21 The results of Kraft lignin solubility in HEAL, BHEAL and THEAL at 323.15 K are presented in

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2
3 Figure 3. The Kraft lignin solubility values and the corresponding standard deviations are also
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5 presented in Table S3 in ESI.
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4 **Figure 3.** Kraft lignin solubility in neat HEAL, BHEAL, and THEAL (all at 5 wt%
5 water content) at 323.15 K.

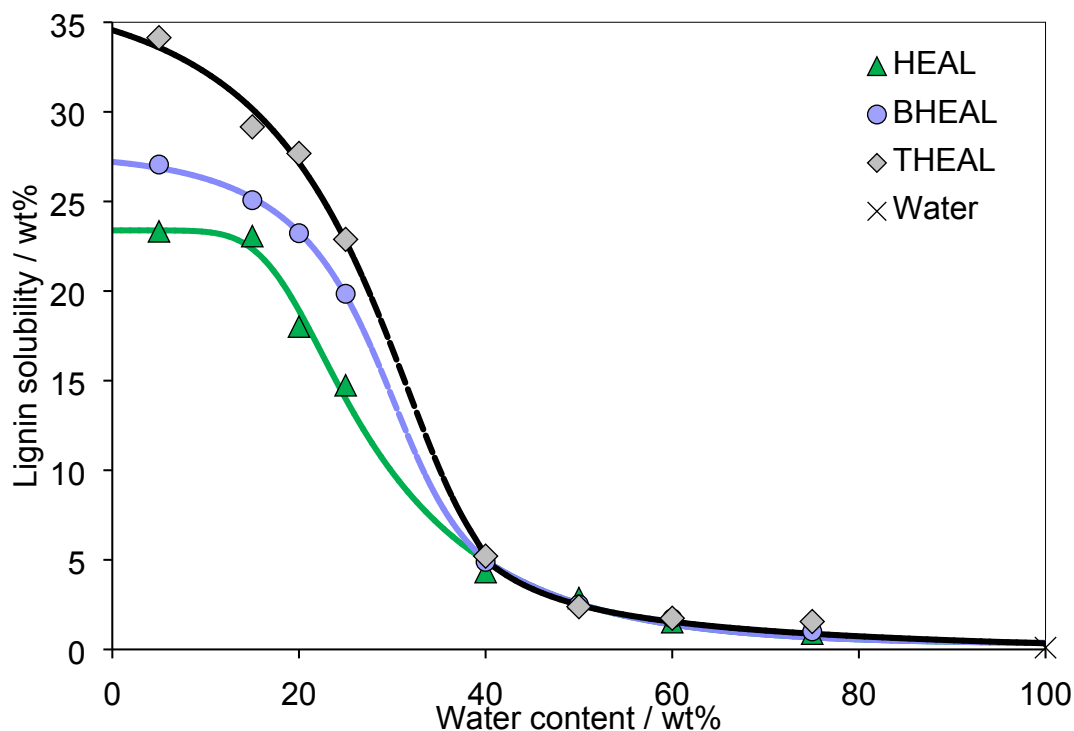
6
7 The results presented in Figure 3 show that the PILs capacity to dissolve Kraft lignin is also
8 affected by the cationic part. The Kraft lignin solubility increased in the following sequence:
9 THEAL > BHEAL > HEAL; indicating that larger alkanolammonium-based cations in
10 combination with lactate anion are capable of dissolving a higher lignin concentration.
11 Surprisingly, this trend is opposite to that observed in our previous study where smaller
12 alkanolammonium-based cation conjugated with propionate anion allowed for a better Kraft
13 lignin dissolution.⁴⁶ These different behaviors lead to further investigation on the correlation of
14 the chemical nature of the PILs with the Kraft lignin solubility.

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3 1 PILs are easily synthesized by a proton transfer from an organic acid to an organic base,
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6 2 thus both ionic and neutral species are generally present in equilibrium.³⁴ Some studies
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8
9 3 demonstrate that the extension of proton transfer is associated with the pKa values of the neutral
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11 4 species (acid and base). The larger the ΔpK_a ($pK_a(\text{base}) - pK_a(\text{acid})$) the higher is the proton
12
13 5 transfer favoring the formation of ionic species to the detriment of neutral species.^{56,57} As reported
14
15
16 6 in Table 1. Purities, chemical structures and suppliers of the pure bases and acids used
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18
19 7 in this study 2-hydroxyethylamine presents the highest pKa (9.5), while tris(2-
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22 8 hydroxyethyl)amine presented the lowest value (7.76) among the studied bases. In this
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25 9 context, the proton transfer is more likely to occur at higher extent with 2-
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28 10 hydroxyethylamine than in case of tris(2-hydroxyethyl)amine. This argument is
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32 11 supported by Stoimenovski et al. (2010) that investigated the extent of proton transfer during
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34
35 12 the synthesis of primary and ternary ammonium-based PILs using acetic acid as precursor.⁵⁸ The
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37 13 authors concluded that primary amines resulted in full proton transfer, while ternary amines
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39 14 presented relatively little proton transfer (only a partial reaction occurred, with the presence of
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41 15 the parent acid and base molecules). These conclusions were qualitatively supported by the
42
43 16 Walden plot and by the deprotonation study of an acid indicator performed by researchers⁵⁸.
44
45 17 According to Stoimenovski et al. (2010), primary ammonium-based PILs exhibited a Walden plot
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47 18 behavior close to ideal line (deviation lower than 8%), while ternary ammonium-based PILs
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49 19 presented deviations larger than 23%.⁵⁸ Having this in mind, it would be expected more mass
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51 20 fraction of ionic species in HEAL and HEAP than in case of THEAL and THEAP. To a further
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53 21 investigation about the different behaviors observed in this study (HEAL, BHEAL, and THEAL)
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55 22 and in our previous study reported (HEAP, BHEAP, THEAP),⁴⁶ the solubility of lignin in pure
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1 acids (lactic and propionic) and bases (2-hydroxyethylamine, bis(2-hydroxyethyl)amine and
2 tris(2-hydroxyethyl)amine) were investigated.

3 In order to exploit the role of neutral species on lignin solubility, the ability of pure molecular
4 solvents (propionic and lactic acids as well as 2-hydroxyethylamine, bis(2-hydroxyethyl)amine
5 and tris(2-hydroxyethyl)amine) to dissolve Kraft lignin was evaluated and the solubility values
6 obtained in these solvents are reported in Table S4 in ESI. The results revealed 14.76 wt% lignin
7 solubility in propionic acid, while lactic acid was capable of dissolving more than twice as much
8 lignin (33.0 wt%) at 323.15 K. In absence of water, the extra hydroxyl group in lactic acid may
9 favors the lignin dissolution by establishing hydrogen bonds with polar groups attached to the
10 lignin structure.^{19,23} On the other hand, the Kraft lignin solubility in amines ranged between
11 28.32 wt% for tris(2-hydroxyethyl)amine, and 31.04 wt% for (2-hydroxyethylamine), which is
12 not a significant variation. Based on these results, it can be inferred that in case of
13 alkanolammonium-based PILs with propionate the ionic species favor lignin dissolution where
14 the ability of dissolving lignin (HEAP > BHEAP > THEAP) correlates with the higher extension
15 of proton transfer.⁴⁶ On the opposite, the less extension of proton transfer in THEAL favored
16 lignin dissolution to the detriment of HEAL with a higher proton transfer extent.

17 Concerning the effect of water on lignin solubility (Figure 4 and Table S3), its anti-solvent role
18 influences negatively lignin solubility in all cases. Furthermore, no significant differences
19 between the PILs aqueous solutions ability to dissolve lignin was observed at water concentrations
20 higher than 40 wt%, suggesting that the cationic part of PIL affects mainly the lignin solubility
21 for low water contents (<40 wt%).⁴⁶ These results indicate that the cationic part plays a secondary
22 role, while the anionic counterpart (Section 3.1) is the major player in the PILs lignin dissolution
23 process, as previously reported.^{46,55,59,60}



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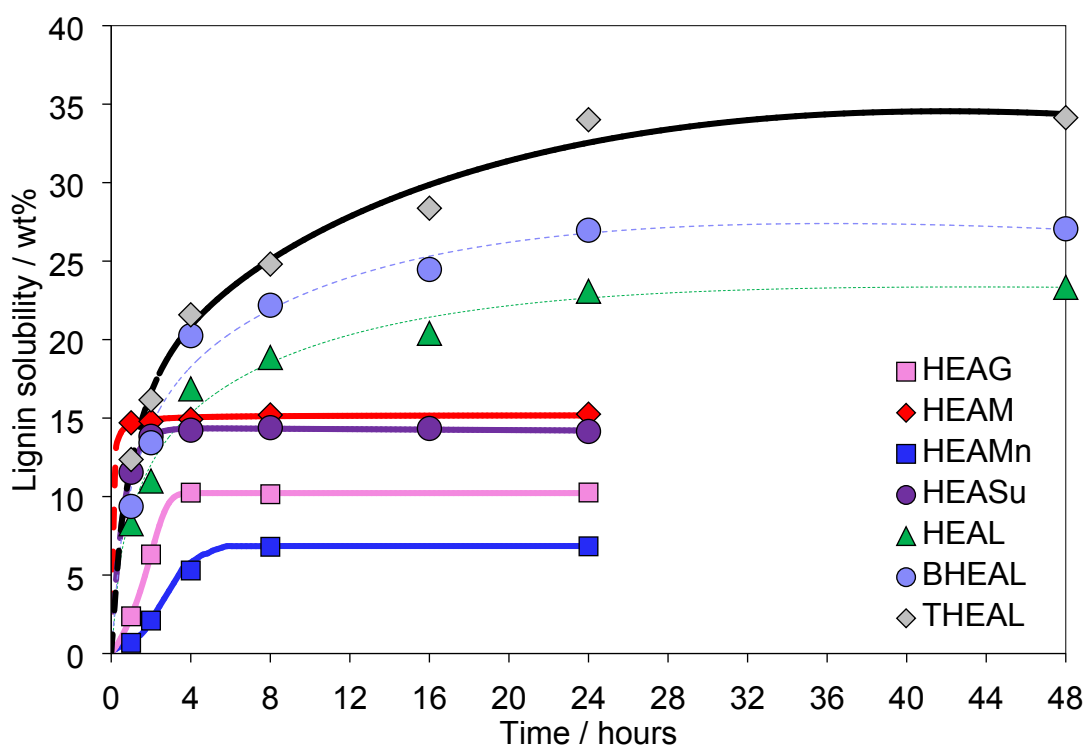
2 **Figure 4.** Kraft lignin solubility in HEAL, BHEAL and THEAL aqueous solutions
3 and pure water at 323.15 K. Lines are guide for eyes.

4

5 *3.3 Time-dependence of Kraft lignin dissolution in PILs*

6 Time is a key factor to achieve economical success in industrial-scale processes for
7 which the goal is to reach a maximum production in the shortest time. The influence of
8 time on lignin dissolution is presented in Figure 5. The assays were performed with PILs
9 aqueous solutions containing 5 wt% of water at 323.15 K. Exceptionally, the water
10 content in HEASu was equal to 20 wt% for the reasons previously mentioned. The

1 solubility of Kraft lignin and the respective standard deviations are presented in Table S5
2 in ESI.



3

4 **Figure 5.** Time-dependent dissolution of Kraft lignin in PILs (95 wt%) at 323.15 K.

5 Lines are guide for eyes.

6

7 Two different dissolution behaviors can be observed in Figure 5. The HEAM achieved almost
8 saturation after only 1 hour of stirring. Besides, a short time was required to achieve the maximum
9 lignin solubility for HEASu (2 hours), while 4 and 8 hours were necessary to saturate the system
10 for HEAG and HEAMn, respectively. Amongst all studied solvents, lactate-based PILs took the
11 longest time (24 hours) to achieve saturation.

12 The lignin dissolution in HEASu was fast and more than 81% of maximum solubility was reached
13 in just 1 hour. The HEAM exhibited an even higher dissolution rate, achieving more than 96% of
14 the maximum solubility in 1 h. On the other hand, a slower dissolution rate was observed for

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3 1 HEAG and more pronounced for HEAMn. For example, it was required, approximately, 1.7 and
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5 2 2.7 hours to achieve half of maximum lignin solubility value for HEAG and HEAMn,
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7 3 respectively. This behavior may be attributed to the poorer ability of these PILs to dissolve lignin,
8
9 4 but also to their viscosity (Table S7 - ESI). Since HEAMn presents a higher viscosity than HEAG
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11 5 it is expected that the lignin dissolution process would take longer. Initially, the HEAM presents
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13 6 fast dissolution rate, and after 1 hour of experiment this rate abruptly reduces achieving the
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15 7 saturation through a slow and progressive dissolution that may be attributed to the high viscosity
16
17 8 of HEAM which is more viscous at 323.15 K (almost 3-fold) than any other PIL used in this
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19 9 study. It was achieved 14.7 wt% of lignin solubility after 1 hour in HEAM, and after this point, a
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21 10 slow dissolution rate (0.07 wt% of lignin dissolution per hour) was observed until saturation was
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23 11 achieved, approximately 8 hours after the experiment start. This high viscosity may impair the
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25 12 mass transfer process, and consequently decreases the lignin dissolution rate at this final step. ⁶¹⁻
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27 13 ⁶³
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29 14 As demonstrated above, some PILs took a long time (over 24 hours) to reach saturation using
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31 15 mechanical agitation (with a magnetic bar), which could be associated to the inefficient agitation
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33 16 provided by this method for viscous solvents. Therefore, the possibility of decreasing the time
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35 17 required to fully dissolve lignin was investigated. The Kraft lignin solubility in selected PILs,
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37 18 namely HEAMn, HEAG and THEAL, were performed using ultrasounds at 323.15 K. The lignin
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39 19 solubilities are represented in Figure 6, and in Table S6 in ESI along with the respective standard
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41 20 deviations.
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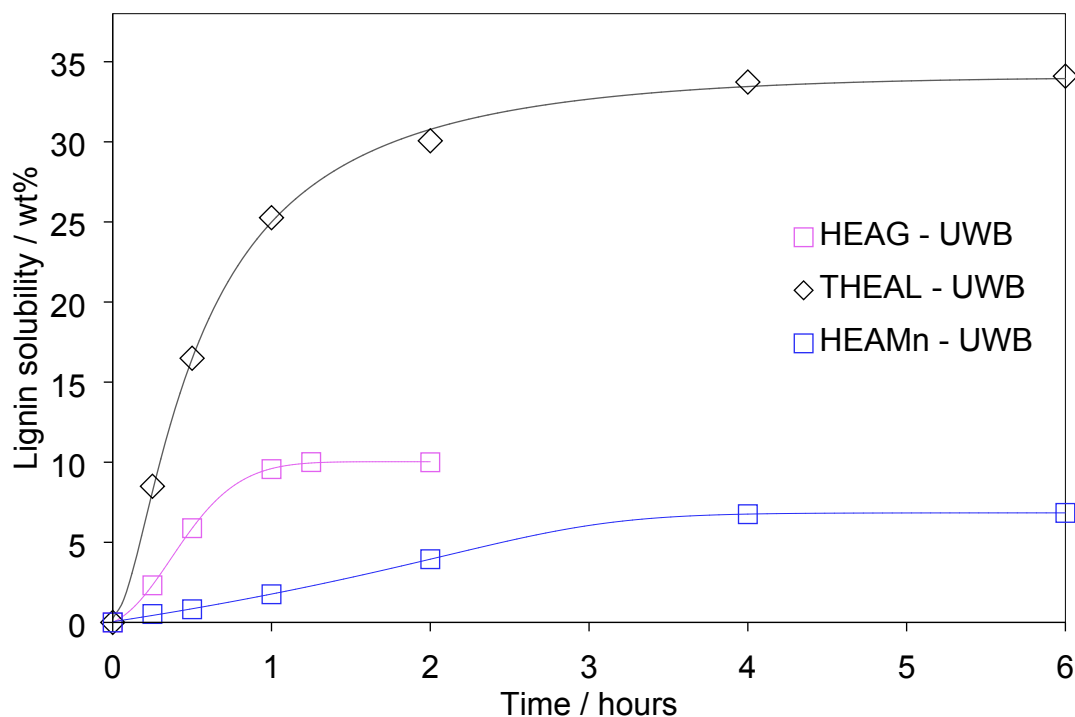


Figure 6. Time-dependent dissolution of lignin in PILs (95 wt%) at 323.15 K using an ultrasound water bath (UWB). Lines are guide for eyes.

The data obtained with ultrasound agitation showed that lignin saturation was achieved within 1.25 hours with HEAG, while 4 hours were needed for both HEAMn and THEAL.

These dissolution rates were much higher than those observed with mechanical agitation (Figure 5), in which periods of time between 8 and 24 hours were needed to reach maximal lignin solubility in these PILs. Therefore, the use of PILs in combination with ultrasounds seems to be a fast and efficient method to dissolve Kraft lignin at low temperature (323.15 K).

3.4 The effect of temperature on Kraft lignin solubility

THEAL was chosen to study the effect of temperature on Kraft lignin dissolution, since it presented the best dissolution performance among all PILs here investigated (Sections 3.1 and 3.2). The Kraft lignin solubility in pure water, in THEAL and its aqueous solutions at 313.15, 323.15, 333.15 and 353.15 K are shown in Figure 7. The Kraft lignin solubility values and corresponding standard deviations are presented in Table S8 in ESI.

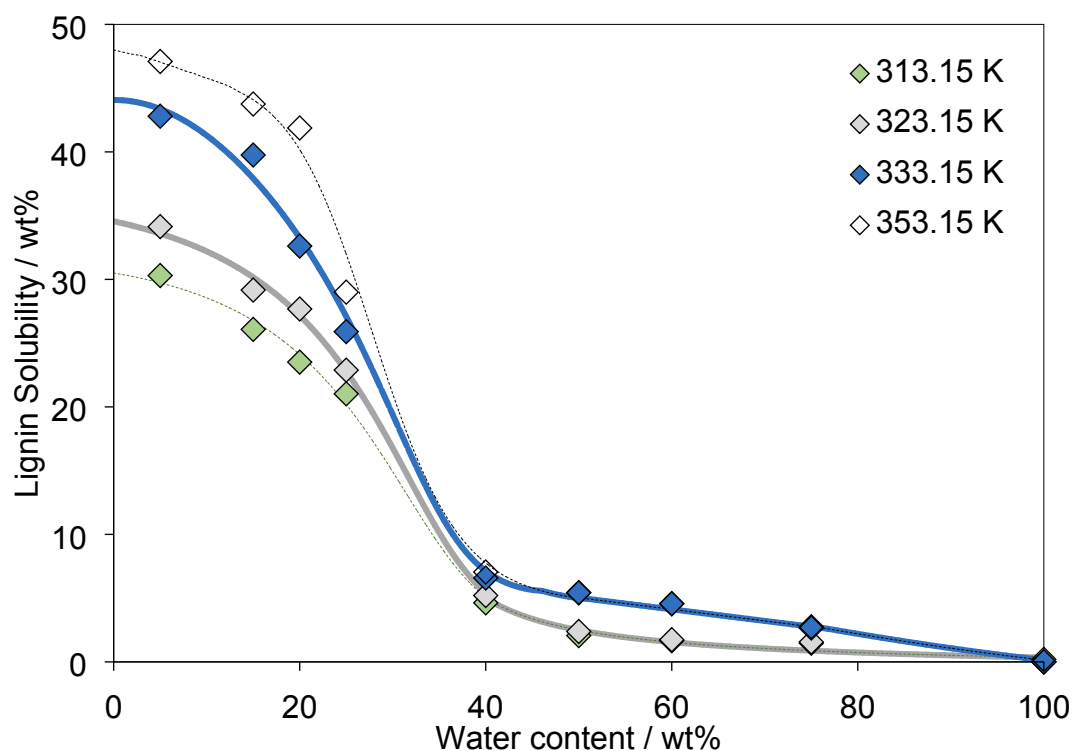


Figure 7. Kraft lignin solubility in THEAL aqueous solutions and pure water at 313.15, 323.15, 333.15 and 353.15 K. Lines are guide for eyes.

As depicted in Figure 7, all lignin solubility curves presented the same trend: the temperature increase enhanced the lignin solubility, especially at water concentrations lower than 25 wt%. On the other hand, the lignin solubility in PIL aqueous solutions containing high water content (> 40 wt%) is poorly sensitive to the temperature increase.

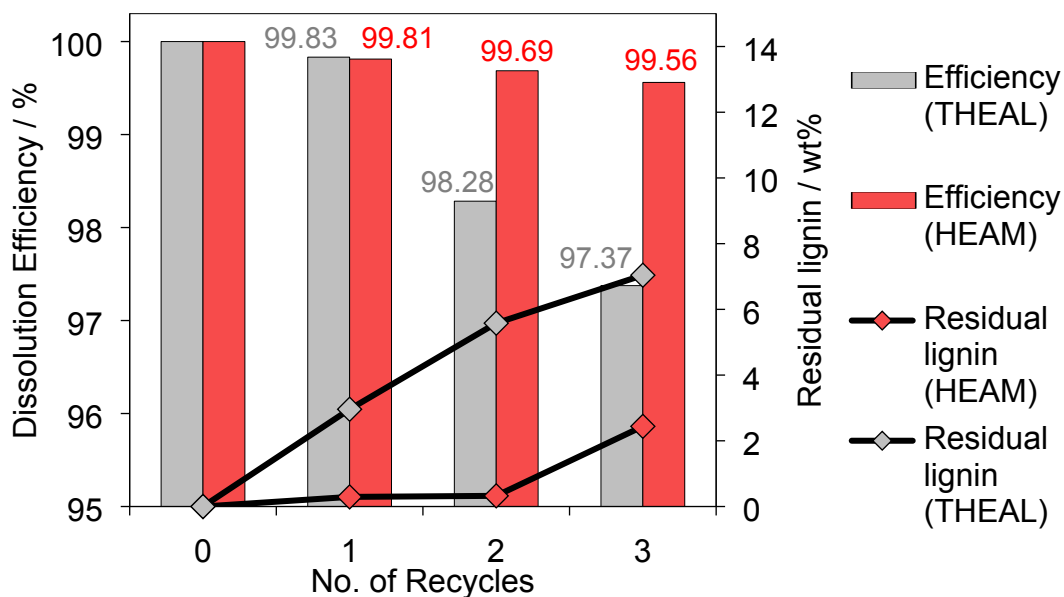
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3 1 The trends observed in solubility curves explain the anti-solvent role of water that
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6 2 solvates the PIL ions and hinders their interaction with lignin. This also helps explaining
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9 3 why temperature has a low impact on lignin solubility in high water content, while the
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12 4 opposite is observed for concentrated PILs where strong interactions are established
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16 5 between PIL ions and lignin that are reinforced by the temperature increase.
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20 6 THEAL demonstrated to be an excellent solvent for lignin reaching a maximum of 47.09
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23 7 wt% lignin solubility at 353.15 K (Figure 7). This is a noteworthy value achieved with a
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26 8 lower temperature than that reported in similar studies using other solvents. ^{27,28,50,64–66}
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32 33 34 35 10 *3.5 Recycling of PIL*

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37 11 The recycling of PILs is crucial to achieve an economical and sustainable process. Some
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40 12 authors have reported the recovery of PILs after lignin extraction or dissolution through
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43 13 vacuum distillation. ^{20,24,26,67} In this study, the HEAM and THEAL were chosen, as proof
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46 14 of concept, to demonstrate the possibility of recovering and reusing PILs after lignin
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49 15 dissolution.
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54 16 The recycling step was performed as described in Section 2.6 and up to 93 wt% and up
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57 17 to 96 wt% of the initial HEAM and THEAL mass after the distillation process was
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3 1 recovered, respectively, and this loss may be associated to the impregnation of lignin
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6 2 with PILs. The recovered PILs were subsequently used in three cycles of lignin solubility
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9 3 and recovery, and the dissolution efficiencies were compared to the dissolution with fresh
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12 4 PIL (Figure 8). Therefore, a negligible loss in the dissolution efficiencies was
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15 5 demonstrated over the recycling steps for both PILs tested. Besides, a residual lignin
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18 6 content of 0.29, 0.32, and 2.44 wt% was quantified in recycled HEAM for cycles 1, 2, and
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22 7 3, respectively, and 2.96, 5.58, and 7.04 wt% in recycled THEAL for cycles 1, 2, and 3,
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25 8 respectively. The recovered PIL solution becomes darker at the end of each cycle, what
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28 9 is a visual indication that lignin fraction remains dissolved in the solution, probably a low
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32 10 molecular weight lignin as reported in a previous study.⁴⁶
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2 **Figure 8.** Dissolution efficiency of lignin in HEAM and THEAL (95 wt%) and three times
 3 recycled HEAM and recycled THEAL (95 wt%). Residual lignin was determined in
 4 recycled PILs by UV method.

5

6 4. Conclusions

7 A comprehensive study on the ability of alkanolammonium PILs and their aqueous
 8 solutions to dissolve Kraft lignin at low temperatures was performed. The results showed
 9 that the anionic part of PILs influences sharply the lignin dissolution process in these
 10 solvents, while the cationic part plays a secondary role, and that in presence of water
 11 the PIL ions are solvated impairing their interactions with lignin, decreasing its dissolution
 12 ability. The kinetics of dissolution was also investigated and the saturation state was

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3 1 achieved within 8 hours to all PILs tested in study, except to lactate-based PILs, which
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6 2 needed 24 hours to complete the dissolution process. Nevertheless, it was shown that
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10 3 ultrasounds could be used for the dissolution of lignin, allowing faster lignin dissolution
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13 4 when compared to the mechanical agitation with a magnetic bar. The ultrasound is
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16 5 capable to reach lignin saturation within 4 hours, while at least 8 hours are needed with
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19 6 mechanical agitation to achieve the same result. The effect of the temperature was also
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22 7 demonstrated using THEAL and their aqueous solutions, and, as expected, it was
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25 8 observed that the temperature favored the lignin dissolution. This PIL was the best PIL
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28 9 tested in this work to dissolve Kraft lignin, achieving more than 47 wt% lignin solubility at
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31 10 353.15 K. At last, the recycle and reuse of HEAM and of THEAL was successfully
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35 11 demonstrated without losing its efficiency, for at least 3 cycles.
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57 18 the scope of the projects CICECO-Aveiro Institute of Materials, UIDB/50011/2020 &
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24 7 **Supporting information description**
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27 8 PILs characterization (FT-IR, ¹H-NMR and ¹³C-NMR); Calibration curves – Kraft lignin; Kraft
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29 9 lignin solubility in PILs aqueous solutions at 323.15 K; Viscosity of neat PILs at different
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31 10 temperatures; Kraft lignin solubility in THEAL aqueous solutions at 313.15, 323.15, 333.15 and
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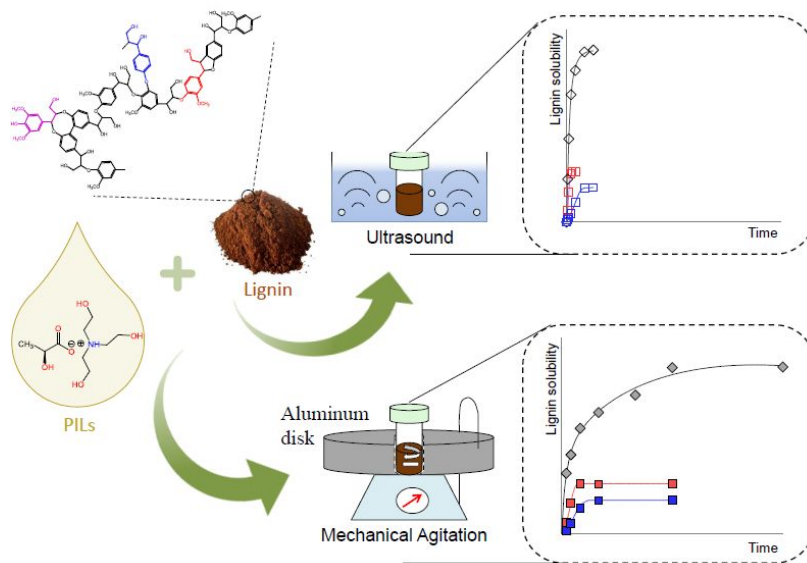
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