Supporting Information

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MANUSCRIPT TITLE: Hydrotropy and co-solvency on lignin solubilization in deep eutectic solvents

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METHODOLOGY

New method to quantify the technical lignin solubility in DES. The most conventional analytical method for the quantification of dissolved technical lignins is ultraviolet spectroscopy at 280 nm, where the lignin absorbance follows the Beer-Lambert Law.[1] This method require a solids free samples with low concentration of analyte. However, in the technical lignin solubility assays, after reach the saturation in both neat DES and in aqueous solution, due to the dark color and the high viscosity of the solutions it was not possible to filtrate or centrifuge the samples in order to separate the two phases. Therefore, this condition precludes the analysis and quantification of lignin solubility in DES by UV-vis spectroscopy. To overcome this limitation, the Fourier-transform infrared (FTIR) spectroscopy emerge as another analytical technique, that has been shown to be a powerful tool for quantitative lignin analysis in solutions.[1] This technique allow the fast analysis of liquid or solid using an attenuated total reflection (ATR) accessory. In that sense, three technical lignins obtained from different delignification processes (kraft, organosolv and alkali lignins) were selected and analyzed by FTIR spectroscopy accoupled with ATR cell. The FTIR normalized spectra are depicted in Figure S1. The absorption bands were assigned as suggested by O. Faix.[2]

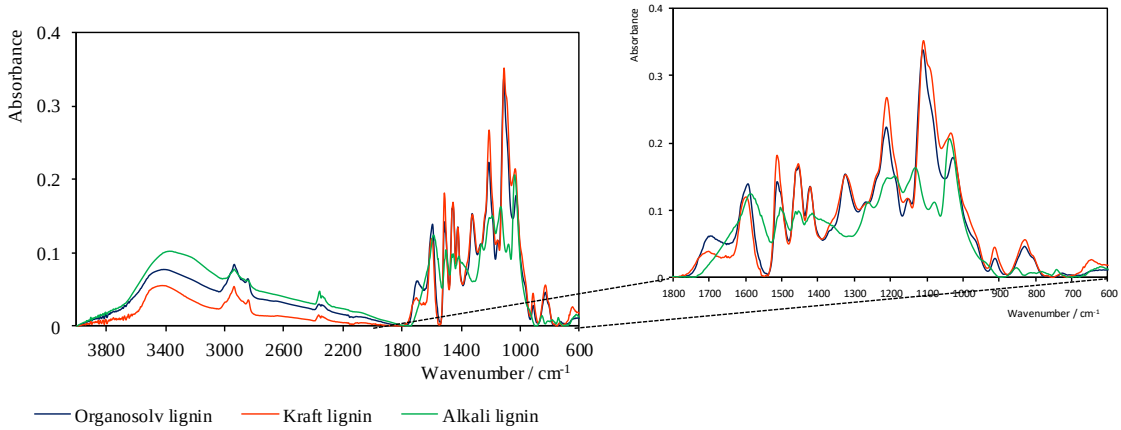

Figure S1. FTIR normalized spectrum of technical lignins obtained from different delignification processes of *Eucalyptus globulus* wood.

Figure S1, shows the FTIR spectra of some typical technical lignins. Commom features as well as particular vibrations, specific of each lignin, are found in the spectra. In the case of the technical lignins selected for this study, the FTIR spectra show a broad band at 3400 cm^{-1} attributed to the hydroxyl groups in phenolic and aliphatic structures (O-H stretching), and the bands centred around 2930 and 2830 cm^{-1}, predominantly arising from C-H stretching in methyl and methylene groups. In the carbonyl/carboxyl region, a band is observed at 1710 cm^{-1}, originating from unconjugated carbonyl/carboxyl C=O stretching (this band was absent in the spectra of alkali lignin). Aromatic skeletal vibration at 1594, 1510 and 1424 cm^{-1} and the C-H deformation combined with aromatic ring vibration at 1460 cm^{-1}, are commom for all lignins, although the intensity of the bands may differ.

The spectral region below 1400 cm^{-1} is more difficult to analyse, since most bands are complex, with contribution from various vibration modes. The spectra of kraft and organosolv lignins show a band at 1316 cm^{-1}, which is characteristic for syringyl (S) ring plus (G) ring condensed and at 1269 cm^{-1} for guaiacyl (G) ring plus C=O stretching, observed for all lignins spectra. A strong vibration at 1214 cm^{-1}, only observed for kraft and organosolv lignins spectra, can be associated with C-C plus C-O plus C=O stretching. A shoulder at 1145 cm^{-1} assigned to the aromatic C-H in-plane deformation guaiacyl-type

and a strong band at 1107 cm^{-1} characteristic of C-O deformation in secondary alcohols and aliphatic ethers. The spectra of all lignin samples show at 1035 cm^{-1} assigned to the aromatic C-H in-plane deformation, plus C-O deformation in primary alcohols and plus C=O stretch. Finally, the bands at 918 and 822 cm^{-1} are associated with the aromatic C-H out-of-plane deformation, only observed in kraft and organosolv lignin FTIR spectra.

Considering that all technical lignins showed the band at 1510 cm^{-1}, characteristic of aromatic skeletal vibrations in FTIR normalized spectra, a new methodology was implemented to quantify their solubility in DES (neat and in aqueos solution) at this specific band. This band is the most convenient in the region of 1500 – 600 cm^{-1}. The 1594 cm^{-1} lignin band is difficult to use because of water band interference at 1625 cm^{-1} and the interference of carboxyl band at 1698 cm^{-1} from carboxylic acid-based DES.

Therefore, it was possible to build the calibration cuves using the three technical lignins dissolved in different neat DES at 353.15 K and different lignin concentrations (until 42 wt % for organosolv and 13 wt % for kraft and alkali lignins, to avoid the saturation point). The neat DES, EG:[Ch]Cl (2:1), EG:[N_{2222}]Cl (2:1) and EG:[N_{4444}]Cl (2:1) were selected because negligible absorbance, correspondig to the water content in neat DES, were observed in their FTIR normalized spectra in the especific range of 1600 – 1500 cm^{-1} (see Figure S2). Furthermore, considering the good performance of PA:U (2:1) on technical lignin solubilization, demonstrated in our previous work,[3] we decide to introduce the correlation of different kraft lignin concentration dissolved in PA:U (2:1) at 353.15 K with their respective absorbance after FTIR analysis. The objective was to evaluate their influence on the calibration curve, taken into account that PA:U (2:1) present an significant absorbance in the range of 1800 – 1500 cm^{-1}, as observed in their FTIR normalized spectra (see Figure S2), associated with the stretching vibration of carboxyl group from propionic acid (PA).

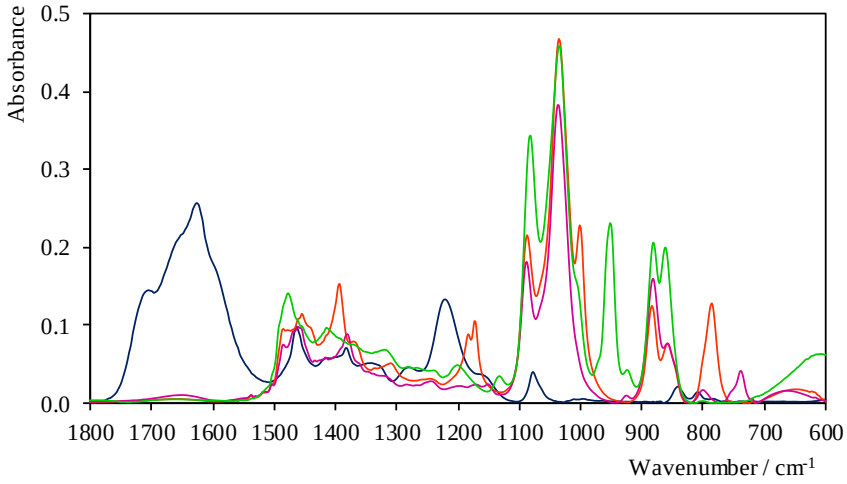

Figure S2. FTIR normalized spectrum of neat DES, EG:[Ch]Cl (2:1) (green), EG:[N_{2222}]Cl (2:1) (orange), EG:[N_{4444}]Cl (2:1) (pink) and PA:U (2:1) (blue).

Figure S3 (left), ilustrate the correlation between technical lignins concentrations in four different pure DES and the respective absorbance obtained from FTIR spectroscopy analysis at 1510 cm^{-1}. In the case of polyols-based DES, these results shows that independently of the HBA used to prepare DES (with EG as common HBD), no significant influences were observed in the curve, at the same conditions. The sligth data dispersion observed below 15 wt % of technical lignin dissolved in DES, are possibly related to the different technical lignins chemical structures, associated with the different isolation procces, affecting consequently their solubilization. In the case of kraft lignin disssolved in carboxylic acid-based DES, the results showed an slight increase of absorbance, when compared with the kraft lignin dissolved in polyols-based DES. These differences can be associated with the interference of carboxyl group absorbance in the region of our analysis (1600 – 1500 cm^{-1}), as observed in Figure S2. Nevertheless, it was possible to obtain a good linearity with high statistical significance at the 95 % confidence level, considering all data (see Figure S3, right).

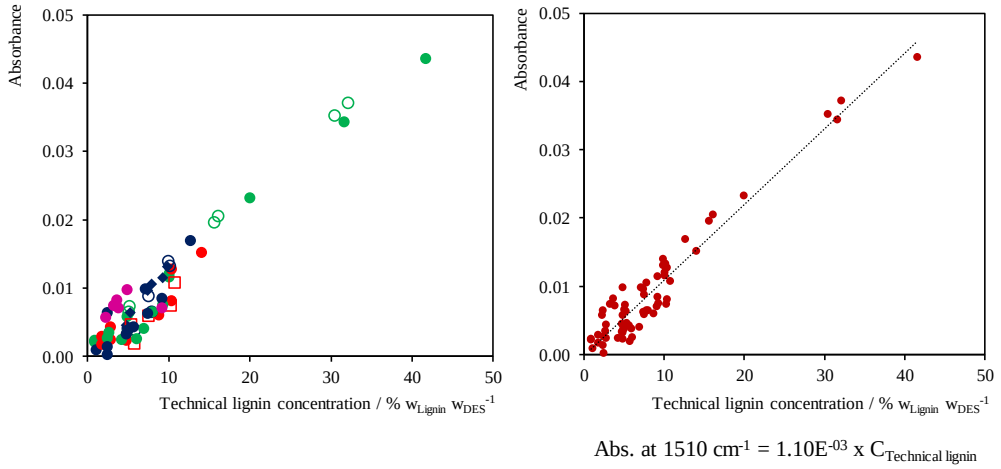

Figure S3. Correlation between technical lignins concentration (alkali lignin – red, organosolv lignin – green and kraft lignin – blue) dissolved in different neat DES (EG:[Ch]Cl (2:1) – dot; EG:[N_{4444}]Cl (2:1) – circle; EG:[N_{2222}]Cl (2:1) – square, and PA:U (2:1) – pink dot) at 353.15 K and the respective absorbance, analyzed by FTIR spectroscopy at 1510 cm^{-1} (left) and Calibration curve of technical lignins in these neat DES at 353.15 K, considering all data (right).

The regression coefficient, their uncertainty associated, correlation coefficient, and the ANOVA analysis are reported in Table S1.

Table S1. Regression analysis of technical lignins calibration curve, analyzed by FTIR spectroscopy at 1510 cm^{-1}.

m / % w_{DES} w_{Lignin}^{-1}	σ	CI_m	R	Predicted R^2	Adjusted R^2	t-statistic	p-value
$1.10E^{-03}$	$3.76E^{-05}$	$6.89E^{-03}$	$9.83E^{-01}$	$9.67E^{-01}$	$9.51E^{-01}$	$4.34E^{+01}$	$3.47E^{-49}$

m, slope; σ, standard deviation (error) of the gradient; CI_m, confidence interval (95 %) of the gradient; R, correlation coefficient and R^2, correlation coefficient square.

The correlation coeficient (R) or Pearson *R* value[4,5] (R=0.983) provides a measure of the degree to which the values of lignin concentration and the absorbance of lignin dissolved in DES are lineary correlated. The parameters related to R are the predicted R^2 and the adjusted R^2. The predicted R^2 describe the fraction of the total variance in the data which is contributed by the fitted regression line.[5] In this study, a predicted R^2 of 0.967 means that the data are well-correlated and the best-fit line describes the data. The adjusted R^2 is useful for assessing the effect of adding additional terms to the equation of

the fitted line.[5] In this case, the adjusted R^2 of 0.951 is in agreement with the predicted R^2 of 0.967, than we concluded that it is no needed additional terms. Finally, the confidence limitis for the slope are $1.10E^{-03} \pm 3.76E^{-05}$, this represent the extremes of the value that the slope could take, at the 95 % confidence level. Regarding the ANOVA analysis, the *t*-statistic value of 43.4 implies the model is significant and the *p*-value less than 0.05 (in this case, $3.47E^{-49}$) indicate that the model terms are also significant.

Regarding the residual analysis, their assumptions: independence (lack of correlation) of error, homoscedasticity (constant variance) of erros and normality of the error distribution, are depicted in Figure S4. The residuals normal distributions can be observed in the predicted versus experimental absorbance plot and the normal probability plot, because in a normal distribution the residual are in a straight line. Moreover, the residual plot (residual versus lignin concentration) show that the erro have constant variance, with the residulas scatteres randomly around zero, so assuming that the erros terms have a mean of zero is reasonable. In that sense, we concluded that all the assumptions were successfully verified.

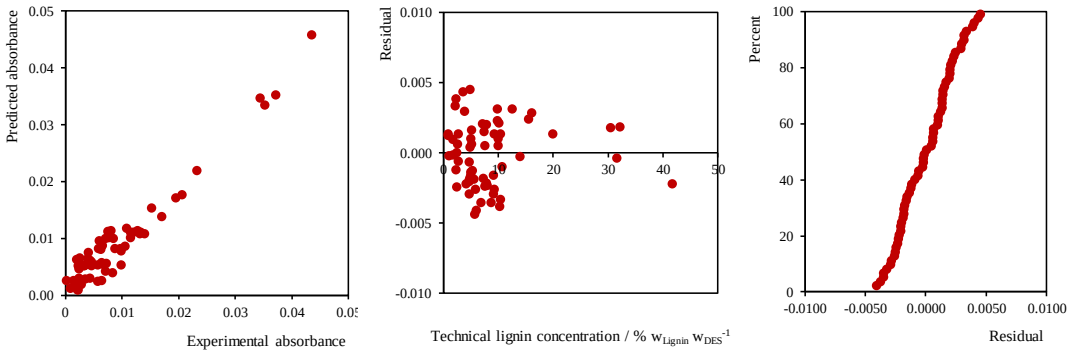

Figure S4. Regression analysis of dissolved technical lignins in neat DES: correlation between the predicted and experimental absorbance (left), residual plot (center) and normal probability plot (right).

The calibration curve validation with two test samples. The validation of analytical methods is a requirement for the quality and comparability of analytical results. For this purpose, two different samples of kraft lignin at two different concentrations (a) 5 wt % and (b) 7 wt % dissolved in neat EG:[Ch]Cl (2:1) at 353.15 K, were prepared and analyzed by two different methodologies (FTIR spectroscopy and gravimetrical techniques) to quantify the lignin concentration, in order to validate the calibration curve.

Regarding the methodologies used, the FTIR analysis was carried out following the same procedure previously described. The gravimetrical analyses, after reach the total solubilization of lignin in DES at 353.15 K, the sample was filtrated to separate some solid residue from the liquid phase (this solid was dried until constant weight). After that, the lignin was isolated from the liquid phase adding cool water overnight, to promote the flocculation and sedimentation of dissolved lignin. The lignin isolated, was collected after filtration and dried at 303.15 K in an oven with vacuum, until constant weight. The lignin that remain in liquid phase was quantified by UV-vis spectroscopy, using an alkali lignin calibration curve in water, because is the lignin more soluble in water when compared with organosolv and kraft lignins (see Figure S5). The detail values of lignin concentration obtained from each methodology, are reported in Table S2.

Table S2. Experimental lignin concentration obtained from FTIR spectroscopy at 1510 cm^{-1} and gravimetrical analysis.

FTIR analysis

Sample	DES / g	Lignin / g	Lignin concentration / % w_{Lignin} w_{DES}^{-1}	Absorbance at 1510 cm^{-1}	Lignin concentration from calibration curve / % w_{Lignin} w_{DES}^{-1}
a	0.5246	0.0261	4.98	0.00384	**3.49**
b	0.5334	0.0392	7.35	0.00623	**5.66**

Gravimetrical analysis (GA)

Sample	DES / g	Lignin / g	Lignin concentration / % w_{Lignin} w_{DES}^{-1}	Residue / g	Isolated lignin / g	Lignin in liquid phase by UV-vis / g	Lignin concentration from GA / % w_{Lignin} w_{DES}^{-1}
a	2.0300	0.1007	4.96	0.02	0.0589	0.0109	**3.44**
b	2.0620	0.1528	7.41	0.03	0.0938	0.0141	**5.23**

As observed in Table S2, it was possible to determine the lignin concentration dissolved in neat DES by two different methodologies, with a difference between them of 0.05 wt % for (a) sample and 0.43 wt % for (b) sample. Furthermore, around 20 wt % of lignin remain insoluble, as demonstrated by the gravimetrical analysis. Despite this fact, these results proved that the FTIR spectroscopy technique can be a powerful tool for quantitative lignin analysis in solutions. Finally, the lignin concentration dissolved in DES was successfully predicted by the proposed calibration curve with statistical significance at 95 % confidence level.

FIGURES

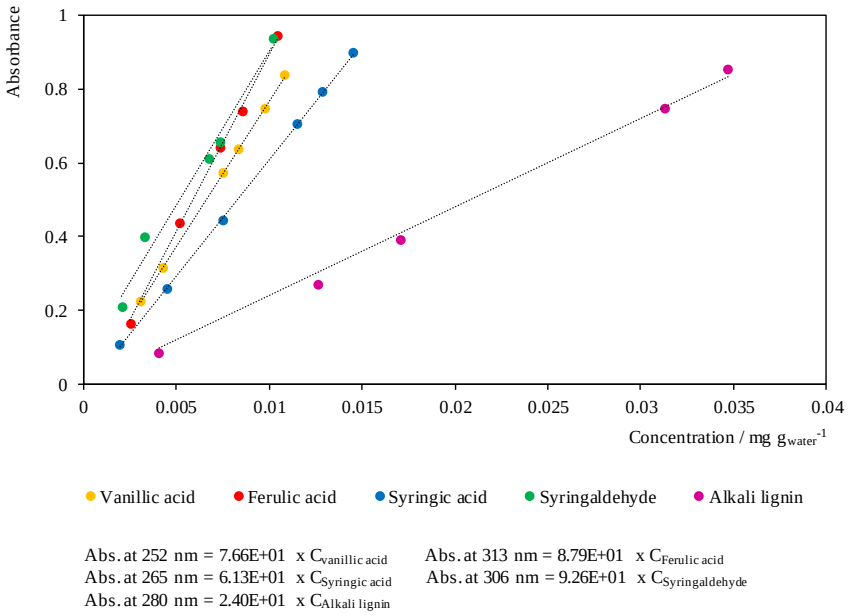

Figure S5. Calibration curves of lignin monomer model compounds and alkali lignin in water at 298.15 K, obtained from UV-vis spectroscopy. Abs, absorbance and C, concentration of lignin monomer model compounds or Alkali lignin. The results of the regression analysis (slope, correlation coefficient and residual standard deviation) are presented in Table S3.

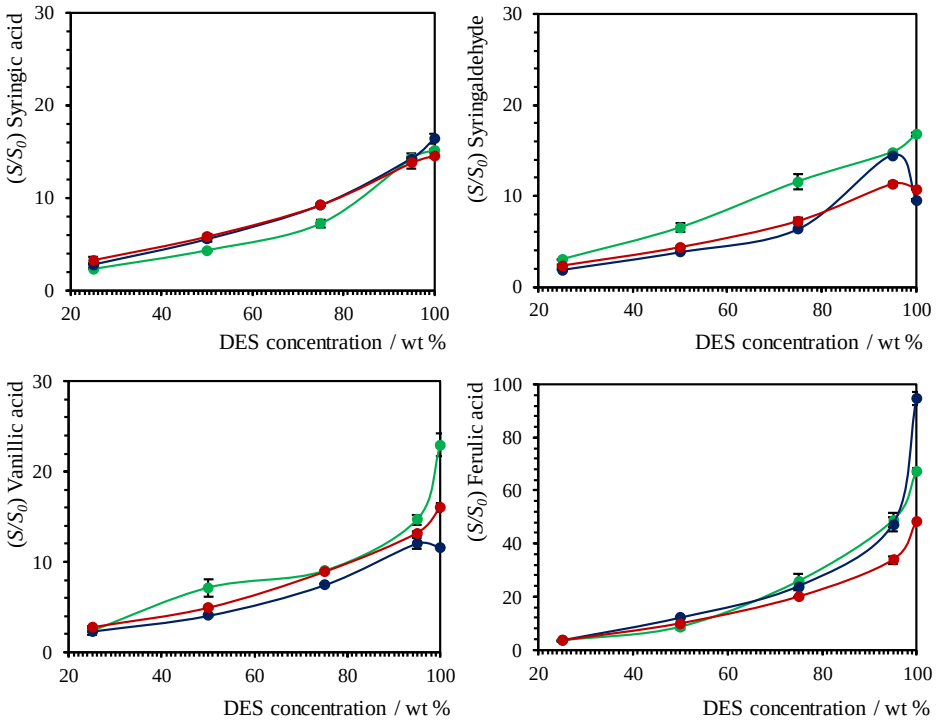

Figure S6. Influence of FA:[Ch]Cl (2:1) concentration and temperature on the solubility enhancement of lignin monomer model compounds (syringaldehyde, and syringic, vanillic and ferulic acids). The different temperatures studied were 303.15 K (green), 313.15 K (blue) and 323.15 K (red).

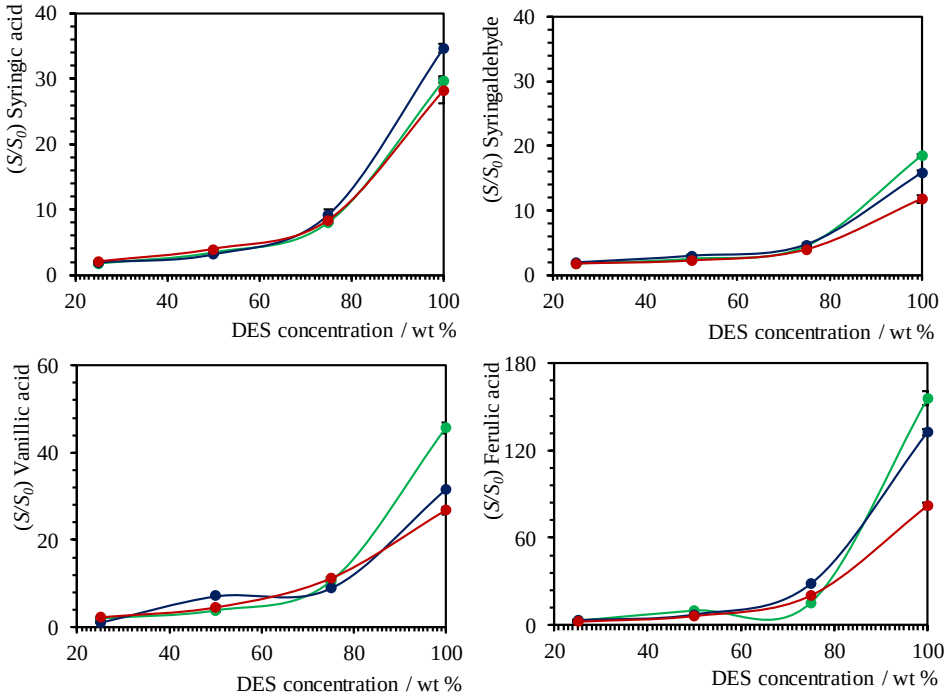

Figure S7. Influence of EG:[Ch]Cl (2:1) concentration and temperature on the solubility enhancement of lignin monomer model compounds (syringaldehyde, and syringic, vanillic and ferulic acids). The different temperatures studied were 303.15 K (green), 313.15 K (blue) and 323.15 K (red).

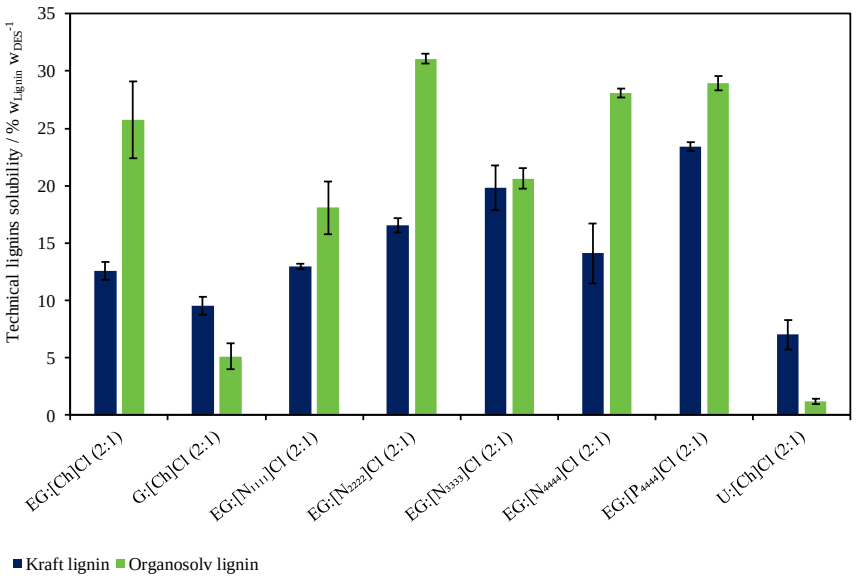

Figure S8. Solubilities of technical lignins in neat polyols-based DES at 353.15 K, obtained from FTIR spectroscopy at 1510 cm^{-1}.

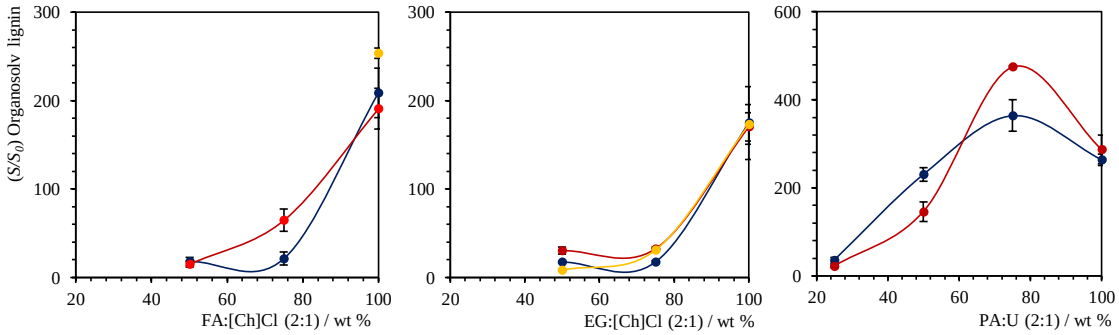

Figure S9. Influence of FA:[Ch]Cl (2:1), EG:[Ch]Cl (2:1) and PA:U (2:1) concentration and temperature on the solubility enhancement of organosolv lignin. The different temperatures studied were 313.15 K (blue), 323.15 K (red) and 353.15 K (yellow).

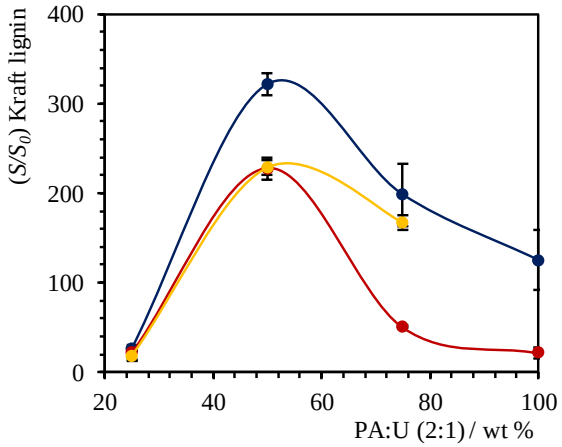

Figure S10. Influence of PA:U (2:1) concentration and temperature on the solubility enhancement of kraft lignin. The different temperatures studied were 313.15 K (blue), 323.15 K (red) and 353.15 K (yellow).

TABLES

Table S3. Regression analysis of lignin monomer model compounds and alkali lignin calibration curves (UV-vis spectroscopy).

	m / g_{water} mg^{-1}	σ	CI_m	R	Predicted R^2	Adjusted R^2	*t-statistic*	*p*-value
Syringaldehyde	9.26E+01	5.92E+00	2.43E-01	9.93E-01	9.86E-01	7.50E-01	96.32	6.96E-08
Vanillic acid	7.66E+01	7.98E-01	3.92E-02	9.99E-01	9.99E-01	8.00E-01	234.86	2.66E-11
Syringic acid	6.13E+01	8.27E-01	5.16E-02	9.99E-01	9.99E-01	8.00E-01	140.80	3.43E-10
Ferulic acid	8.79E+01	3.27E+00	1.49E-01	9.98E-01	9.97E-01	7.50E-01	93.39	7.88E-08
Alkali lignin	2.40E+01	7.07E-01	1.01E-01	9.99E-01	9.98E-01	7.49E-01	56.98	5.68E-07

m, slope; σ, standard deviation (error) of the gradient; CI_m, confidence interval (95 %) of the gradient; R, correlation coefficient and R^2, correlation coefficient square.

Table S4. Experimental solubilities of lignin monomer model compounds in different DES aqueous solutions at 323.15 K, obtained from UV-vis spectroscopy.

Lignin monomer model compounds	Syringic acid		Syringaldehyde		Vanillic acid		Ferulic acid	
	Solubility ± σ / mg g^{-1}	$S/S_0 \pm \sigma$	Solubility ± σ / mg g^{-1}	$S/S_0 \pm \sigma$	Solubility ± σ / mg g^{-1}	$S/S_0 \pm \sigma$	Solubility ± σ / mg g^{-1}	$S/S_0 \pm \sigma$
DES	***FA:[Ch]Cl (2:1)***							
wt % of DES								
0	1.87 ± 0.08	1.00 ± 0.00	7.91 ± 0.76	1.00 ± 0.00	3.24 ± 0.11	1.00 ± 0.00	1.53 ± 0.05	1.00 ± 0.00
25	6.13 ± 0.68	3.28 ± 0.36	18.36 ± 0.98	2.32 ± 0.12	8.95 ± 0.36	2.77 ± 0.11	5.25 ± 0.39	3.43 ± 0.25
50	10.85 ± 0.41	5.82 ± 0.22	34.46 ± 1.22	4.36 ± 0.15	15.91 ± 0.32	4.92 ± 0.10	15.10 ± 0.22	9.87 ± 0.15
75	17.24 ± 0.12	9.24 ± 0.06	57.30 ± 3.14	7.25 ± 0.40	28.72 ± 0.32	8.88 ± 0.10	30.54 ± 0.22	19.96 ± 0.15
95	25.75 ± 1.25	13.81 ± 0.67	89.68 ± 2.08	11.34 ± 0.26	42.64 ± 0.75	13.18 ± 0.23	51.88 ± 2.20	33.91 ± 1.44
100	27.22 ± 0.50	14.59 ± 0.27	85.33 ± 0.38	10.79 ± 0.05	51.77 ± 1.56	16.00 ± 0.48	73.97 ± 0.55	48.35 ± 0.36
	LA:[Ch]Cl (10:1)							
0	1.87 ± 0.08	1.00 ± 0.00	7.91 ± 0.76	1.00 ± 0.00	3.24 ± 0.11	1.00 ± 0.00	0.82 ± 0.03	1.00 ± 0.00
25	6.76 ± 0.48	3.62 ± 0.26	22.21 ± 3.69	2.81 ± 0.47	6.64 ± 1.39	2.05 ± 0.43	4.23 ± 0.57	2.76 ± 0.37
50	9.80 ± 2.47	5.26 ± 1.32	50.32 ± 4.13	6.36 ± 0.52	13.32 ± 2.53	4.12 ± 0.78	12.07 ± 1.56	7.88 ± 1.02
75	13.28 ± 2.45	7.12 ± 1.32	67.12 ± 1.30	8.49 ± 0.16	18.67 ± 1.04	5.77 ± 0.32	16.55 ± 2.33	10.80 ± 1.52
95	15.16 ± 2.89	8.13 ± 1.55	94.42 ± 4.73	11.94 ± 0.60	19.95 ± 0.80	6.16 ± 0.25	27.82 ± 1.61	18.15 ± 1.05
100	16.87 ± 1.96	9.67 ± 1.27	87.83 ± 6.27	11.11 ± 0.79	19.50 ± 2.56	6.03 ± 0.79	26.17 ± 0.82	17.08 ± 0.53
	PA:[Ch]Cl (2:1)							
0	1.87 ± 0.08	1.00 ± 0.00	7.91 ± 0.76	1.00 ± 0.00	3.24 ± 0.11	1.00 ± 0.00	0.82 ± 0.03	1.00 ± 0.00
25	9.89 ± 1.70	5.30 ± 0.91	56.54 ± 1.71	7.15 ± 0.22	15.61 ± 0.30	4.82 ± 0.09	10.59 ± 0.57	6.91 ± 0.37

50	13.20 ± 0.93	7.08 ± 0.50	80.58 ± 0.02	10.19 ± 0.00	38.61 ± 0.22	11.93 ± 0.07	41.10 ± 0.84	26.82 ± 0.55
75	31.50 ± 1.41	16.89 ± 0.76	178.22 ± 40.0	22.54 ± 5.10	63.86 ± 1.39	19.73 ± 0.43	84.54 ± 1.42	55.16 ± 0.92
95	60.47 ± 0.62	32.42 ± 0.33	121.14 ± 10.95	15.32 ± 1.38	85.32 ± 0.73	26.36 ± 0.23	114.97 ± 4.88	75.02 ± 3.19
100	57.23 ± 1.33	30.69 ± 0.71	107.98 ± 6.00	13.65 ± 0.76	95.77 ± 0.19	29.59 ± 0.06	130.89 ± 1.20	85.41 ± 0.78
				PA:U (2:1)				
0	1.87 ± 0.08	1.00 ± 0.00	7.91 ± 0.76	1.00 ± 0.00	3.24 ± 0.11	1.00 ± 0.00	1.53 ± 0.05	1.00 ± 0.00
25	16.94 ± 1.66	9.08 ± 0.89	86.40 ± 3.11	10.93 ± 0.39	20.31 ± 1.57	6.27 ± 0.48	17.60 ± 1.20	11.48 ± 0.79
50	58.02 ± 1.83	36.52 ± 0.59	91.29 ± 2.25	11.54 ± 0.28	51.64 ± 1.99	15.96 ± 0.61	68.99 ± 0.35	45.02 ± 0.23
75	88.37 ± 3.55	47.38 ± 1.90	189.63 ± 2.93	23.98 ± 0.37	52.14 ± 2.20	16.11 ± 0.68	43.50 ± 1.35	28.38 ± 0.88
95	15.86 ± 0.32	8.51 ± 0.17	81.72 ±0.08	10.33 ± 0.01	35.98 ± 1.55	11.12 ± 0.48	13.69 ± 0.93	8.93 ± 0.61
100	11.27 ± 3.11	6.03 ± 1.67	6.95 ± 1.01	0.88 ± 0.13	19.05 ± 0.48	5.89 ± 0.15	8.18 ± 0.00	5.34 ± 0.00
				PTSA:[Ch]Cl (1:1)				
0	1.87 ± 0.08	1.00 ± 0.00	7.91 ± 0.76	1.00 ± 0.00	3.24 ± 0.11	1.00 ± 0.00	0.82 ± 0.03	1.00 ± 0.00
25	8.05 ± 1.10	4.32 ± 0.59	29.93 ± 3.92	3.78 ± 0.50	11.84 ± 0.48	3.66 ± 0.15	4.50 ± 0.52	2.94 ± 0.34
50	13.07 ± 1.18	7.01 ± 0.63	53.62 ± 3.54	6.78 ± 0.45	16.13 ± 0.04	4.98 ± 0.01	7.35 ± 0.11	4.80 ± 0.07
75	15.82 ± 1.6	8.48 ± 0.89	64.09 ± 4.47	8.10 ± 0.57	19.49 ± 1.11	6.02 ± 0.34	18.82 ± 1.09	12.28 ± 0.71
95	24.93 ± 1.06	13.37 ± 0.57	63.60 ± 0.00	8.04 ± 0.00	34.72 ± 4.85	10.73 ± 1.50	17.88 ± 0.94	11.66 ± 0.61
100	33.80 ± 1.50	18.12 ± 0.80	78.99 ± 0.00	9.99 ± 0.00	45.19 ± 0.00	13.96 ± 0.00	16.75 ± 0.19	10.93 ± 0.12
				EG:[Ch]Cl (2:1)				
0	1.87 ± 0.08	1.00 ± 0.00	7.91 ± 0.76	1.00 ± 0.00	3.24 ± 0.11	1.00 ± 0.00	1.53 ± 0.05	1.00 ± 0.00
25	3.78 ± 0.11	2.03 ± 0.06	14.05 ± 0.88	1.78 ± 0.11	7.17 ± 0.30	2.21 ± 0.09	3.64 ± 0.26	2.38 ± 0.17
50	7.37 ± 0.15	3.95 ± 0.08	17.74 ± 0.64	2.24 ± 0.08	14.47 ± 1.31	4.47 ± 0.41	9.55 ± 0.52	6.23 ± 0.34
75	15.71 ± 0.18	8.43 ± 0.10	31.37 ± 0.83	3.97 ± 0.11	35.99 ± 0.71	11.12 ± 0.22	31.18 ± 0.05	20.34 ± 0.03
95	34.49 ± 0.17	18.49 ± 0.09	51.95 ± 1.46	6.57 ± 0.18	78.69 ± 1.25	24.32 ± 0.39	94.81 ± 5.94	61.86 ± 3.88
100	52.81 ± 3.75	28.31 ± 2.01	93.28 ± 4.68	11.80 ± 0.59	86.61 ± 2.89	26.76 ± 0.89	125.70 ± 3.19	82.02 ± 2.08
				EG:[P_{4444}]Cl (2:1)				
0	1.87 ± 0.08	1.00 ± 0.00	7.91 ± 0.76	1.00 ± 0.00	3.24 ± 0.11	1.00 ± 0.00	0.82 ± 0.03	1.00 ± 0.00
25	39.98 ± 0.09	26.09 ± 0.06	113.37 ± 9.14	14.34 ± 1.16	57.85 ± 8.62	17.87 ± 2.66	192.71 ± 4.72	125.74 ± 3.08
50	115.39 ± 0.66	75.29 ± 0.43	200.07 ± 32.51	25.30 ± 4.11	116.85 ± 3.36	36.11 ± 1.04	310.32 ± 25.82	202.48 ± 16.85
75	178.74 ± 2.51	116.63 ± 1.64	275.84 ± 53.11	34.88 ± 6.72	189.77 ± 1.47	58.64 ± 0.45	287.35 ± 2.37	187.50 ± 1.54
95	166.98 ± 0.00	94.31 ± 0.00	264.46 ± 58.55	33.44 ± 7.40	192.07 ± 8.19	59.35 ± 2.53	211.30 ± 22.60	137.87 ± 14.75
100	165.27 ± 6.79	88.62 ± 3.64	218.79 ± 31.67	27.67 ± 4.00	195.97 ± 6.60	60.55 ± 2.04	*	*
				U:[Ch]Cl (2:1)				
0	1.87 ± 0.08	1.00 ± 0.00	7.91 ± 0.76	1.00 ± 0.00	3.24 ± 0.11	1.00 ± 0.00	0.82 ± 0.03	1.00 ± 0.00
25	11.77 ± 0.46	6.31 ± 0.25	19.52 ± 1.68	2.47 ± 0.21	11.21 ± 0.77	3.46 ± 0.24	15.76 ± 0.95	10.28 ± 0.62
50	19.52 ± 1.81	10.47 ± 0.97	27.31 ± 4.52	3.45 ± 0.57	18.23 ± 0.67	5.63 ± 0.21	14.13 ± 0.65	13.69 ± 1.42
75	14.13 ± 0.65	7.58 ± 0.35	5.51 ± 0.89	0.70 ± 0.11	26.28 ± 1.01	8.12 ± 0.31	14.30 ± 1.51	9.33 ± 0.99

95	9.74 ± 0.08	5.22 ± 0.04	4.05 ± 0.18	0.51 ± 0.02	24.30 ± 0.28	7.51 ± 0.09	9.51 ± 0.45	6.20 ± 0.30
100	10.17 ± 0.13	5.45 ± 0.07	1.60 ± 0.47	0.20 ± 0.06	*	*	6.66 ± 1.74	4.34 ± 1.14

σ, standard deviation; S, the solubility of lignin monomer model compounds in the aqueous solutions of DES; S_0, the solubility of lignin monomer model compounds in pure water; *, the high viscosity of sample hampers the filtration and consequently the analysis.

Table S5. Experimental solubilities of lignin monomer model compounds in FA:[Ch]Cl 2:1 aqueous solutions at three different temperatures, obtained from UV-vis spectroscopy.

Lignin monomer model compounds	Syringic acid		Syringaldehyde		Vanillic acid		Ferulic acid	
	Solubility ± σ / mg g^{-1}	$S/S_0 \pm \sigma$	Solubility ± σ / mg g^{-1}	$S/S_0 \pm \sigma$	Solubility ± σ / mg g^{-1}	$S/S_0 \pm \sigma$	Solubility ± σ / mg g^{-1}	$S/S_0 \pm \sigma$
T / K				***303.15***				
wt % of DES								
0	1.28 ± 0.01	1.00 ± 0.00	2.92 ± 0.01	1.00 ± 0.00	1.83 ± 0.06	1.00 ± 0.00	0.63 ± 0.06	1.00 ± 0.00
25	2.96 ± 0.08	2.31 ± 0.06	8.88 ± 0.12	3.04 ± 0.04	4.35 ± 0.05	2.37 ± 0.03	2.18 ± 0.10	3.47 ± 0.17
50	5.54 ± 0.18	4.32 ± 0.14	19.09 ± 1.43	6.54 ± 0.49	13.08 ± 1.77	7.14 ± 0.97	5.43 ± 0.54	8.62 ± 0.86
75	9.25 ± 0.48	7.22 ± 0.38	33.83 ± 2.58	11.58 ± 0.88	16.49 ± 0.11	9.00 ± 0.06	16.28 ± 1.67	25.87 ± 2.65
100	19.37 ± 0.25	15.11 ± 0.20	49.07 ± 0.59	16.81 ± 0.20	42.04 ± 2.34	22.93 ± 1.27	42.40 ± 0.68	67.37 ± 1.08
				313.15				
0	1.60 ± 0.03	1.00 ± 0.00	4.41 ± 0.10	1.00 ± 0.00	2.93 ± 0.06	1.00 ± 0.00	0.82 ± 0.03	1.00 ± 0.00
25	4.51 ± 0.09	2.82 ± 0.06	8.42 ± 0.17	1.91 ± 0.04	6.88 ± 1.05	2.35 ± 0.36	2.83 ± 0.06	3.45 ± 0.07
50	8.87 ± 0.46	5.55 ± 0.29	16.96 ± 0.07	3.85 ± 0.02	11.94 ± 0.34	4.08 ± 0.11	9.82 ± 0.06	11.98 ± 0.08
75	14.72 ± 0.03	9.21 ± 0.02	28.08 v 0.08	6.37 ± 0.02	21.80 ± 0.49	7.45 ± 0.17	19.56 ± 1.13	23.85 ± 1.38
100	26.21 ± 0.80	16.39 ± 0.50	42.01 ± 0.28	9.53 ± 0.06	33.94 ± 0.60	11.60 ± 0.20	77.60 ± 2.06	94.64 ± 2.51
				323.15				
0	1.87 ± 0.08	1.00 ± 0.00	7.91 ± 0.76	1.00 ± 0.00	3.24 ± 0.11	1.00 ± 0.00	1.53 ± 0.05	1.00 ± 0.00
25	6.13 ± 0.68	3.28 ± 0.36	18.36 ± 0.98	2.32 ± 0.12	8.95 ± 0.36	2.77 ± 0.11	5.25 ± 0.39	3.43 ± 0.25
50	10.85 ± 0.41	5.82 ± 0.22	34.46 ± 1.22	4.36 ± 0.15	15.91 ± 0.32	4.92 ± 0.10	15.10 ± 0.22	9.87 ± 0.15
75	17.24 ± 0.12	9.24 ± 0.06	57.30 ± 3.14	7.25 ± 0.40	28.72 ± 0.32	8.88 ± 0.10	30.54 ± 0.22	19.96 ± 0.15
100	27.22 ± 0.50	14.59 ± 0.27	85.33 ± 0.38	10.79 ± 0.05	51.77 ± 1.56	16.00 ± 0.48	73.97 ± 0.55	48.35 ± 0.36

σ, standard deviation; S, the solubility of lignin monomer model compounds in the aqueous solutions of DES; S_0, the solubility of lignin monomer model compounds in pure water.

Table S6. Experimental solubilities of lignin monomer model compounds in EG:[Ch]Cl 2:1 aqueous solutions at three different temperatures, obtained from UV-vis spectroscopy.

Lignin monomer model compounds	Syringic acid		Syringaldehyde		Vanillic acid		Ferulic acid	
	Solubility ± σ / mg g^{-1}	$S/S_0 \pm \sigma$	Solubility ± σ / mg g^{-1}	$S/S_0 \pm \sigma$	Solubility ± σ / mg g^{-1}	$S/S_0 \pm \sigma$	Solubility ± σ / mg g^{-1}	$S/S_0 \pm \sigma$
T / K				***303.15***				
wt % of DES								
0	1.28 ± 0.01	1.00 ± 0.00	2.92 ± 0.01	1.00 ± 0.00	1.83 ± 0.06	1.00 ± 0.00	0.63 ± 0.06	1.00 ± 0.00
25	2.25 ± 0.12	1.76 ± 0.09	5.12 ± 0.42	1.75 ± 0.14	3.44 ± 0.12	1.88 ± 0.07	1.68 ± 0.02	2.67 ± 0.03
50	4.43 ± 0.11	3.46 ± 0.09	7.24 ± 0.42	2.48 ± 0.14	6.82 ± 0.20	3.72 ± 0.11	6.11 ± 0.13	9.71 ± 0.21
75	10.35 ± 0.04	8.07 ± 0.03	13.06 ± 0.18	4.47 ± 0.06	19.04 ± 0.02	10.39 ± 0.01	9.56 ± 0.30	15.20 ± 0.48
100	38.11 ± 0.43	29.73 ± 0.34	53.94 ± 0.76	18.47 ± 0.26	83.71 ± 2.43	45.66 ± 1.32	98.09 ± 2.96	155.85 ± 4.70
				313.15				
0	1.60 ± 0.03	1.00 ± 0.00	4.41 ± 0.10	1.00 ± 0.00	2.93 ± 0.06	1.00 ± 0.00	0.82 ± 0.03	1.00 ± 0.00
25	3.12 ± 0.22	1.95 ± 0.14	8.16 ± 0.08	1.85 ± 0.02	3.17 ± 0.39	1.08 ± 0.13	2.58 ± 0.24	3.13 ± 0.30
50	5.08 ± 0.01	3.18 ± 0.01	12.72 ± 0.82	2.89 ± 0.19	20.81 ± 0.06	7.11 ± 0.02	5.78 ± 0.14	7.01 ± 0.16
75	14.81 ± 1.19	9.26 ± 0.74	20.58 ± 1.09	4.67 ± 0.25	26.09 ± 0.41	8.92 ± 0.14	23.26 ± 0.40	28.22 ± 0.48
100	55.54 ± 1.03	34.74 ± 0.65	69.68 ± 1.53	15.81 ± 0.35	92.52 ± 0.69	31.62 ± 0.24	109.28 ± 1.60	132.54 ± 1.93
				323.15				
0	1.87 ± 0.08	1.00 ± 0.00	7.91 ± 0.76	1.00 ± 0.00	3.24 ± 0.11	1.00 ± 0.00	1.53 ± 0.05	1.00 ± 0.00
25	3.78 ± 0.11	2.03 ± 0.06	14.05 ± 0.88	1.78 ± 0.11	7.17 ± 0.30	2.21 ± 0.09	3.64 ± 0.26	2.38 ± 0.17
50	7.37 ± 0.15	3.95 ± 0.08	17.74 ± 0.64	2.24 ± 0.08	14.47 ± 1.31	4.47 ± 0.41	9.55 ± 0.52	6.23 ± 0.34
75	15.71 ± 0.18	8.43 ± 0.10	31.37 ± 0.83	3.97 ± 0.11	35.99 ± 0.71	11.12 ± 0.22	31.18 ± 0.05	20.34 ± 0.03
100	52.81 ± 3.75	28.31 ± 2.01	93.28 ± 4.68	11.80 ± 0.59	86.61 ± 2.89	26.76 ± 0.89	125.70 ± 3.19	82.02 ± 2.08

σ, standard deviation; S, the solubility of lignin monomer model compounds in the aqueous solutions of DES; S_0, the solubility of lignin monomer model compounds in pure water.

Table S7. Experimental solubilities of technical lignins (kraft and organosolv lignins) in different neat DES at 353.15 K, obtained from FTIR spectroscopy at 1510 cm^{-1}.

Technical lignins	kraft lignin	organosolv lignin
	Solubility ± σ / % w_{Lignin} w_{DES}^{-1}	Solubility ± σ / % w_{Lignin} w_{DES}^{-1}
DES		
FA:[Ch]Cl (2:1)	8.10 ± 1.28	37.81 ± 0.88
LA:[Ch]Cl (10:1)	8.59 ± 0.51	*
PA:[Ch]Cl (2:1)	6.00 ± 0.00	28.68 ± 2.96

PA:U (2:1)	23.86 ± 1.03	31.04 ± 0.85
BA:U (2:1)	4.21 ± 0.44	13.27 ± 0.13
PPA:[Ch]Cl (2:1)	7.47 ± 0.51	15.07 ± 1.99
PTSA:[Ch]Cl (1:1)	7.46 ± 0.51	*
EG:[Ch]Cl (2:1)	12.56 ± 0.76	25.74 ± 3.33
G:[Ch]Cl (2:1)	9.54 ± 0.79	5.13 ± 1.16
EG:[N_{1111}]Cl (2:1)	12.96 ± 0.21	18.07 ± 2.30
EG:[N_{2222}]Cl (2:1)	16.54 ± 0.66	31.07 ± 0.45
EG:[N_{3333}]Cl (2:1)	19.80 ± 1.96	20.61 ± 0.89
EG:[N_{4444}]Cl (2:1)	14.12 ± 2.62	28.10 ± 0.40
EG:[P_{4444}]Cl (2:1)	23.40 ± 0.37	28.93 ± 0.61
U:[Ch]Cl (2:1)	7.01 ± 1.26	1.18 ± 0.23

σ, standard deviation; S, the solubility of technical lignin in neat DES; S_0, the solubility of technical lignin in pure water; *, insufficient organosolv lignin to make the solubility test.

Table S8. Experimental solubilities of technical lignins in different DES aqueous solutions at 353.15 K, obtained from FTIR spectroscopy at 1510 cm^{-1}.

Technical lignin	kraft lignin		organosolv lignin	
	Solubility ± σ / % w_{Lignin} w_{DES}^{-1}	$S/S_0 \pm \sigma$	Solubility ± σ / % w_{Lignin} w_{DES}^{-1}	$S/S_0 \pm \sigma$
DES	***FA:[Ch]Cl (2:1)***			
wt % of DES				
0	0.12 ± 0.01	1.00 ± 0.00	0.10 ± 0.00[a]	1.00 ± 0.00[a]
25	2.20 ± 0.93	18.12 ± 7.70	*	*
50	4.82 ± 0.54	39.72 ± 4.47	1.52 ± 0.34[a]	14.71 ± 3.29[a]
75	6.89 ± 1.85	56.79 ± 15.25	6.68 ± 1.32[a]	64.64 ± 12.74[a]
100	8.10 ± 1.28	66.70 ± 10.52	19.72 ± 2.38[a]	190.80 ± 23.05[a]
	LA:[Ch]Cl (10:1)			
0	0.12 ± 0.01	1.00 ± 0.00	0.15 ± 0.02	1.00 ± 0.00
25	0.61 ± 0.19	4.98 ± 1.92	*	*
50	1.07 ± 0.03	8.84 ± 0.28	*	*
75	3.47 ± 0.96	28.54 ± 7.89	*	*
100	8.59 ± 0.51	70.76 ± 4.23	*	*
	PA:[Ch]Cl (2:1)			
0	0.12 ± 0.01	1.00 ± 0.00	0.15 ± 0.02	1.00 ± 0.00
25	1.13 ± 0.39	9.30 ± 3.23	*	*
50	8.41 ± 0.74	72.98 ± 6.42	*	*

75	12.19 ± 0.39	100.42 ± 3.19	*	*
100	6.00 ± 0.00	49.41 ± 0.04	28.68 ± 2.96	192.51 ± 19.86
	PA:U (2:1)			
0	0.12 ± 0.01	1.00 ± 0.00	0.10 ± 0.00[a]	1.00 ± 0.00[a]
25	2.25 ± 0.68	18.50 ± 5.59	2.24 ± 0.28[a]	21.69 ± 2.74[a]
50	27.73 ± 1.00	228.28 ± 8.24	15.06 ± 2.34[a]	145.70 ± 22.66[a]
75	20.37 ± 1.00	167.71 ± 8.26	49.06 ± 0.28[a]	474.74 ± 2.69[a]
100	+	+	+	+
	BA:U (2:1)			
0	0.12 ± 0.01	1.00 ± 0.00	0.15 ± 0.02	1.00 ± 0.00
25	5.41 ± 0.76	44.54 ± 6.27	9.36 ± 0.15	62.79 ± 0.98
50	20.97 ± 3.37	172.65 ± 27.72	15.71 ± 0.52	105.47 ± 3.47
75	15.09 ± 0.31	124.22 ± 2.57	11.52 ± 1.16	77.30 ± 7.79
100	4.21 ± 0.44	34.69 ± 3.62	13.27 ± 0.13	89.05 ± 0.86
	PTSA:[Ch]Cl (1:1)			
0	0.12 ± 0.01	1.00 ± 0.00	0.15 ± 0.02	1.00 ± 0.00
25	1.58 ± 0.33	13.08 ± 2.71	*	*
50	3.72 ± 0.87	30.63 ± 7.18	*	*
75	4.13 ± 0.38	33.99 ± 3.15	*	*
100	10.64 ± 1.98	87.59 ± 16.30	*	*
	EG:[Ch]Cl (2:1)			
0	0.12 ± 0.01	1.00 ± 0.00	0.15 ± 0.02	1.00 ± 0.00
25	1.12 ± 0.18	9.19 ± 1.47	1.91± 0.70	12.82 ± 4.72
50	1.60 ± 0.50	13.16 ± 4.14	1.23 ± 0.13	8.27 ± 0.86
75	7.51 ± 0.69	61.82 ± 5.71	4.63 ± 0.24	31.07 ± 1.61
100	12.56 ± 0.76	103.38 ± 6.30	25.75 ± 3.33	172.78 ± 22.36
	EG:[N_{3333}]Cl (2:1)			
0	0.12 ± 0.01	1.00 ± 0.00	0.15 ± 0.02	1.00 ± 0.00
25	2.86 ± 0.66	23.52 ± 5.47	2.40 ± 0.68	16.08 ± 5.40
50	6.60 ± 1.32	54.37 ± 10.89	13.42 ± 2.82	90.04 ± 10.55
75	9.87 ± 0.67	81.26 ± 5.49	12.41 ± 1.08	83.32 ± 24.35
100	19.80 ± 1.96	163.03 ± 16.12	20.61 ± 1.03	138.32 ± 5.98
	EG:[P_{4444}]Cl (2:1)			
0	0.12 ± 0.01	1.00 ± 0.00	0.15 ± 0.02	1.00 ± 0.00

25	1.39 ± 0.22	11.50 ± 1.82	2.39 ± 0.81	16.08 ± 5.40
50	12.68 ± 0.19	104.41 ± 1.58	8.83 ± 1.60	59.26 ± 10.73
75	15.48 ± 0.10	127.10 ± 1.02	15.13 ± 3.33	101.54 ± 22.34
100	13.77 ± 0.20	113.40 ± 1.00	28.93 ± 0.61	194.17 ± 4.12
		U:[Ch]Cl (2:1)		
0	0.12 ± 0.01	1.00 ± 0.00	0.15 ± 0.02	1.00 ± 0.00
25	1.62 ± 0.73	14.06 ± 6.36	*	*
50	5.66 ± 0.55	46.64 ± 4.54	*	*
75	10.92 ± 0.12	89.87 ± 0.99	*	*
100	7.02 ± 1.26	57.76 ± 10.40	1.18 ± 0.23	7.94 ± 1.53

σ, standard deviation; S, the solubility of technical lignins in the aqueous solutions of DES; S_0, the solubility of technical lignins in pure water; *, insufficient organosolv lignin to make the solubility test; [a], data obtained at 323.15 K; [+], the high viscosity of sample hampers the filtration and consequently the analysis.

Table S9. Experimental solubilities of organosolv lignin in FA:[Ch]Cl (2:1), EG:[Ch]Cl (2:1) and PA:U (2:1) aqueous solutions at three different temperatures, obtained from FTIR spectroscopy at 1510 cm^{-1}.

DES	FA:[Ch]Cl (2:1)		EG:[Ch]Cl (2:1)		PA:U (2:1)	
	Solubility ± σ / % w_{Lignin} w_{DES}^{-1}	$S/S_0 \pm \sigma$	Solubility ± σ / % w_{Lignin} w_{DES}^{-1}	$S/S_0 \pm \sigma$	Solubility ± σ / % w_{Lignin} w_{DES}^{-1}	$S/S_0 \pm \sigma$
T / K			***313.15***			
wt % of DES						
0	0.09 ± 0.00	1.00 ± 0.00	0.09 ± 0.00	1.00 ± 0.00	0.09 ± 0.00	1.00 ± 0.00
25	*	*	*	*	3.06 ± 0.60	35.20 ± 6.80
50	1.56 ± 0.39	18.00 ± 4.50	1.49 ± 0.08	17.21 ± 0.97	19.20 ± 1.33	230.29 ± 15.34
75	1.85 ± 0.63	21.29 ± 7.30	1.60 ± 0.15	17.33 ± 1.76	31.64 ± 3.09	364.41 ± 35.62
100	18.13 ± 2.43	208.80 ± 28.01	15.16 ± 3.57	174.66 ± 41.09	22.94 ± 1.10	264.14 ± 12.73
			323.15			
0	0.10 ± 0.00	1.00 ± 0.00	0.10 ± 0.00	1.00 ± 0.00	0.10 ± 0.00	1.00 ± 0.00
25	*	*	*	*	2.24 ± 0.28	21.69 ± 2.74
50	1.52 ± 0.34	14.71 ± 3.29	3.12 ± 0.41	30.17 ± 4.01	15.06 ± 2.34	145.70 ± 22.66
75	6.68 ± 1.32	64.65 ± 12.74	3.34 ± 0.19	32.35 ± 1.81	49.06 ± 0.28	474.74 ± 2.69
100	19.72 ± 2.38	190.80 ± 23.05	17.60 ± 1.65	170.29 ± 15.98	29.67 ± 3.41	287.11 ± 32.96
			353.15			
0	0.15 ± 0.02	1.00 ± 0.00	0.15 ± 0.02	1.00 ± 0.00	0.15 ± 0.02	1.00 ± 0.00

50	*	*	1.23 ± 0.13	8.27 ± 0.86	*	*
75	*	*	4.63 ± 0.24	31.07 ± 1.61	*	*
100	37.81 ± 0.88	253.77 ± 5.91	25.75 ± 3.33	172.78 ± 22.36	31.04 ± 0.85	206.95 ± 5.68

σ, standard deviation; S, the solubility of organosolv lignin in the aqueous solutions of DES; S_0, the solubility of organosolv lignin in pure water; *, insufficient organosolv lignin to make the solubility test.

Table S10. Experimental solubilities of kraft lignin in PA:U (2:1) aqueous solutions at three different temperatures, obtained from FTIR spectroscopy at 1510 cm^{-1}.

DES	PA:U (2:1)	
	Solubility ± σ / % w_{Lignin} w_{DES}^{-1}	$S/S_0 \pm \sigma$
T / K	***313.15***	
wt % of DES		
0	0.06 ± 0.00	1.00 ± 0.00
25	1.64 ± 0.01	25.95 ± 0.22
50	20.30 ± 0.77	321.66 ± 12.23
75	12.52 ± 2.20	198.43 ± 34.91
100	7.90 ± 2.10	125.28 ± 33.97
	323.15	
0	0.08 ± 0.00	1.00 ± 0.00
25	1.68 ± 0.65	21.83 ± 8.44
50	17.53 ± 0.96	227.74 ± 12.50
75	3.88 ± 0.1	50.34 ± 1.30
100	1.67 ± 0.43	21.63 ± 5.58
	353.15	
0	0.12 ± 0.00	1.00 ± 0.00
25	2.25 ± 0.68	18.50 ± 5.60
50	27.73 ± 1.00	228.28 ± 8.24
75	20.37 ± 1.00	167.71 ± 8.26
100	23.86 ± 1.03	196.40 ± 8.51

σ, standard deviation; S, the solubility of kraft lignin in the aqueous solutions of PA:U (2:1); S_0, the solubility of kraft lignin in pure water.

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