Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

The magic of aqueous solutions of ionic liquids: Ionic liquids as a powerful class of catanionic hydrotropes

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Table S1. Sample summary.

Hydrotrope		Purity (%)	Supplier	NMR spectra	Purification method
Name	Acronym				
1-ethyl-3-methylimidazolium chloride	$[C_1C_2im]Cl$	99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-ethyl-3-methylimidazolium dicyanimide	$[C_2C_1im][N(CN)_2]$	99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-butyl-3-methylimidazolium trifluoromethanesulfonate (triflate)	$[C_4C_1im][CF_3SO_3]$	99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-butyl-3-methylimidazolium thiocyanate	$[C_4C_1im][SCN]$	99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-butyl-3-methylimidazolium methylsulfate	$[C_4C_1im][CH_3SO_4]$	99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-butyl-3-methylimidazolium tosylate	$[C_4C_1im][TOS]$	99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-butyl-3-methylimidazolium bromide	$[C_4C_1im]Br$	99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-butyl-3-methylimidazolium dicyanamide	$[C_4C_1im][N(CN)_2]$	98	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-butyl-3-methylimidazolium chloride	$[C_4C_1im]Cl$	99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-hexyl-3-methylimidazolium chloride	$[C_6C_1im]Cl$	99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-methyl-3-octylimidazolium chloride	$[C_8C_1im]Cl$	99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-decyl-3-decylimidazolium chloride	$[C_{10}C_1im]Cl$	> 99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-dodecyl-3-methylimidazolium chloride	$[C_{12}C_1im]Cl$	> 99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-tetradecyl-3-methylimidazolium chloride	$[C_{14}C_1im]Cl$	> 99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-butyl-3-methylpyridinium dicyanamide	$[C_4C_1py][N(CN)_2]$	> 99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-butyl-1-methylpiperidinium chloride	$[C_4C_1py]Cl$	> 99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-butyl-1-methylpiperidinium chloride	$[C_4C_1pip]Cl$	> 99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
1-butyl-1-methylpyrrolidinium chloride	$[C_4C_1pyrr]Cl$	> 99	Iolitec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
tetrabutylammonium chloride	$[N_{4444}]Cl$	> 99	Sigma-Aldrich	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
tetrabutylphosphonium chloride	$[P_{4444}]Cl$	> 99	Cytec	^1H, ^{13}C	High vacuum (10^{-5} Pa) at 323K

tributylmethylphosphonium tosylate	$[P_{4441}][TOS]$	> 99	Cytec	^{1}H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
cholinium chloride	$[N_{1112(OH)}]Cl$	> 99	Sigma-Aldrich	^{1}H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
tetrabutylammonium tosylate	$[N_{4444}][TOS]$	98	Sigma-Aldrich	^{1}H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
Sodium benzoate	$NaC_7H_5O_2$	> 99	Panreac	^{1}H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
sodium thiocyanate	NaSCN	> 98	Fluka	^{1}H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
sodium chloride	NaCl	> 98	ChemLab	^{1}H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
sodium citrate	$NaC_6H_5O_7$	> 98	JMGS	^{1}H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
sodium tosylate	Na[TOS]	> 95	TCI	^{1}H, ^{13}C	High vacuum (10^{-5} Pa) at 323K
sodium dicyanamide	$Na[N(CN)_2]$	> 96	Sigma-Aldrich	^{1}H, ^{13}C	High vacuum (10^{-5} Pa) at 323K

Table S2. Experimental solubility of vanillin and gallic acid in aqueous solutions of hydrotropes at 303 K ± 0.5 K.

hydrotrope	Weight fraction composition / wt %	vanillin / (g.L^{-1}) solubility ± σ	gallic acid / (g.L^{-1}) solubility ± σ
H_2O	0.00	11.12 ± 0.02	14.38 ± 0.41
[C_4C_1im]Br	5.02		29.58 ± 0.46
	9.98		47.08 ± 1.06
	15.03		49.16 ± 2.95
	19.97		58.52 ± 1.11
[C_4C_1im][CF_3SO_3]	5.03		24.98 ± 0.39
	10.10		37.17 ± 0.72
	15.07		49.38 ± 0.86
	20.02		66.07 ± 3.31
[C_4C_1im][CH_3SO_4]	5.12		28.00 ± 0.85
	9.98		39.83 ± 0.64
	14.99		50.79 ± 3.28
	20.04		82.71 ± 0.51
[C_4C_1im][TOS]	0.84	14.91 ± 0.06	
	2.00	18.04 ± 1.17	
	2.66	20.04 ± 0.35	
	3.37	21.67 ± 0.51	
	4.25	24.94 ± 0.37	
	6.52	36.85 ± 0.82	
	8.08	45.78 ± 0.95	
	10.01	48.43 ± 0.47	47.21 ± 0.66
	19.96	133.06 ± 5.94	84.52 ± 2.36
	50.00	445.60 ± 9.34	
	80.02	402.9 ± 9.38	
	95.01	365.5 ± 10.02	
[C_4C_1py][N(CN)$_2$]	3.00	37.85 ± 1.40	
	5.00	two-phase	56.56 ± 2.74
	10.07		120.59 ± 0.1.08
	15.01		138.57 ± 5.37
	20.02		263.46 ± 1.61
[C_4C_1im][SCN]	4.98		40.80 ± 0.40
	9.94	39.20± 0.41	54.63 ± 0.79
	20.06	two-phase	93.39 ± 1.83
[C_4C_1im][N(CN)$_2$]	5.02		56.46 ± 0.84

	10.06	59.40 ± 2.04	96.52 ± 2.74
	15.02		115.52 ± 3.83
	20.03	two-phase	149.71 ± 0.60
	50.04		329.52 ± 7.35
	74.99		293.61 ± 18.90
	100.00		65.71 ± 6.71
	0.50	14.04 ± 0.17	
	1.00	14.63 ± 0.42	
	1.50	15.77 ± 0.21	
	2.00	16.71 ± 0.58	
	2.50	18.19 ± 0.69	
	4.97	29.16 ± 0.11	34.71 ± 1.69
	7.06		64.02 ± 0.32
$[C_4C_1im]Cl$	9.98	37.03 ± 1.29	64.02 ± 0.32
	12.02		71.79 ± 3.81
	15.01		91.80 ± 0.85
	20.00	89.23 ± 0.92	129.34 ± 5.23
	30.00		
	50.00	369.57 ± 6.67	288.49 ± 6.47
	80.00	374.51 ± 8.17	
	90.00		59.95 ± 3.28
	5.06	24.52 ± 0.58	
	10.09	49.98 ± 0.97	
	14.94	82.12 ± 2.33	
$[C_2C_1im][N(CN)_2]$	20.01	120.7 ± 8.83	
	50.02	394.6 ± 9.50	
	100.00	75.51 ± 3.73	
	5.01	17.58 ± 0.21	
$[C_2C_1im]Cl$	10.03	26.74 ± 0.34	
	15.02	38.89 ± 1.69	
	19.99	45.19 ± 5.61	
$[C_6C_1im]Cl$	10.00	50.02 ± 2.90	
	20.03	152.25 ± 10.00	
	5.00	55.07 ± 3.64	
$[C_8C_1im]Cl$	10.02	91.37 ± 0.78	72.30 ± 1.11
	15.00	117.07 ± 0.36	
	20.01	202.55 ± 2.44	98.68 ± 0.43
	5.00	58.80 ± 1.11	
$[C_{10}C_1im]Cl$	10.00	83.88 ± 6.29	
	20.03	138.36 ± 2.72	
$[C_{12}C_1im]Cl$	5.00	51.49 ± 0.79	
	9.99	66.71 ± 0.42	

	15.00	90.30 ± 9.81	
	19.99	127.06 ± 2.25	
$[C_{14}C_1im]Cl$	5.00	48.17 ± 3.32	
	10.00	70.95 ± 4.70	
	15.00	81.02 ± 8.93	
	20.06	100.28 ± 1.94	
$[C_4C_1py]Cl$	9.98	45.97 ± 0.80	69.28 ± 4.46
	20.01	115.50 ± 10.84	127.00 ± 0.89
$[C_4C_1pyrr]Cl$	10.03	36.48 ± 1.82	67.00 ± 3.93
	20.01	87.60± 3.97	94.68 ± 1.38
$[C_4C_1pip]Cl$	4.95	19.03 ± 1.61	
	9.86	31.38 ± 1.87	52.88 ± 1.31
	14.58	48.49 ± 3.89	
	19.77	76.85 ± 2.97	106.78 ± 5.53
$[N_{1112(}OH)]Cl$	5.00		22.79 ± 0.32
	10.03		28.08 ± 0.21
	15.00		41.19 ± 1.00
	20.01		46.92 ± 1.60
$[N_{4444}]Cl$	9.98	83.62 ± 1.78	4.91 ± 0.90
	20.01	120.32 ± 0.39	3.78± 0.02
$[P_{4444}]Cl$	5.00	33.51 ± 0.99	
	10.02		5.70 ± 0.45
	20.01		3.81 ± 0.17
$Na[C_6H_5O_7]$	10.00	6.16 ± 0.94	41.69 ± 0.84
	19.96	5.07 ± 0.43	39.87 ± 0.90
$Na[C_7H_5O_2]$	5.08	20.83 ± 0.25	
	10.09	31.69 ± 0.66	25.85 ± 2.33
	14.97	52.97 ± 1.28	
	20.04	72.96 ± 4.83	33.16 ± 0.89
Na[SCN]	10.08	14.41 ± 0.51	12.59 ± 0.57
	20.00	23.02 ± 1.60	12.67 ± 1.20
NaCl	9.98	6.19 ± 0.09	10.48 ± 0.02
	20.01	3.28 ± 0.15	6.61 ± 0.08
NaTOS	0.50	13.93 ± 0.28	
	1.00	14.52 ± 0.31	
	1.50	15.45 ± 0.05	
	2.00	16.16 ± 0.11	
	2.50	17.00 ± 0.46	
	5.00	22.76 ± 0.98	
	10.01	34.74 ± 0.88	24.69 ± 0.55
	19.99	84.54 ± 2.09	51.57 ± 0.66
$[N_{4444}][TOS]$	3.00	16.57 ± 0.10	25.74± 0.50

	5.00	16.15 ± 0.15	25.35 ± 0.22
$[P_{4441}][TOS]$	3.00	23.05 ± 0.15	34.78 ± 0.67
	5.00	two phase	
	10.00		
	20.00		

Table S3. Influence of temperature and hydrotrope concentration on the solubility of vanillin

Hydrotrope	wt % of hydrotrope in aqueous solution	T / K		
		303 ± 0.5 K	313 ± 0.5 K	323 ± 0.5 K
$[C_2C_1im][N(CN)_2]$	10.09	49.98 ± 0.97	80.71 ± 3.32	
	20.01	120.7 ± 8.83	159.83 ± 6.91	366.11 ± 22.90
Sodium benzoate	10.09	31.69 ± 0.66	42.92 ± 0.81	181.90 ± 16.94
	20.04	72.96 ± 4.83	110.32 ± 8.10	432.10 ± 27.82

Table S4. Evolution of the agglomerate mean size (diameter in nm) as a function of the solvent (IL and water) addition (series C) and as function of water addition (series D).

Sample	[Van] (mol/L)	[Van]/[IL]	Mean size (d. nm)	Sample	[Van] (mol/L)	[Van]/[IL]	Mean size (d. nm)
C0	0.72	0.548	4.438	D0	0.72	0.548	4.438
C1	0.617	0.47	3.357	D1	0.617	0.548	3.961
C2	0.54	0.411	2.846	D2	0.54	0.547	2.938
C3	0.48	0.365	2.386	D3	0.48	0.548	2.311
C4	0.432	0.339	2.208	D4	0.432	0.548	1.928
C5	0.392	0.299	2.127	D5	0.392	0.547	1.525
				D6	0.36	0.548	1.411
C7	0.332	0.253	2.07	D7	0.332	0.547	1.312

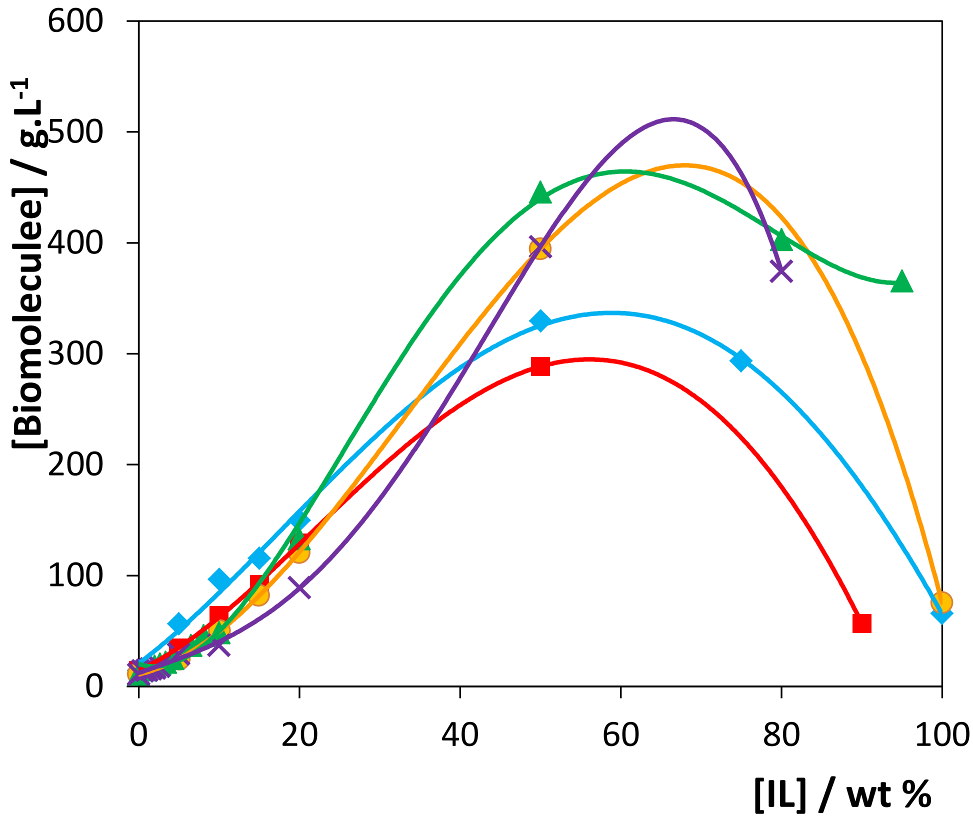
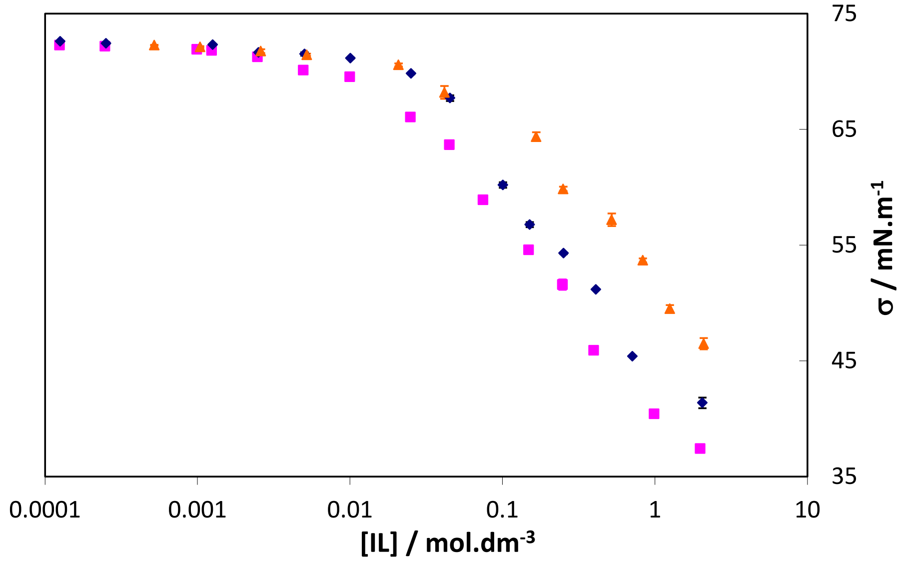


Figure S1. Influence of the concentration of IL on the solubility of gallic acid in aqueous solutions of ◆ $[C_4C_1im][N(CN)_2]$ and ○ $[C_4C_1im]Cl$; vanillin in aqueous solutions of ○ $[C_2C_1im][N(CN)_2]$, ▲ $[C_4C_1im][TOS]$, × $[C_4C_1im]Cl$ at 303 K. Lines are guides for the eye.



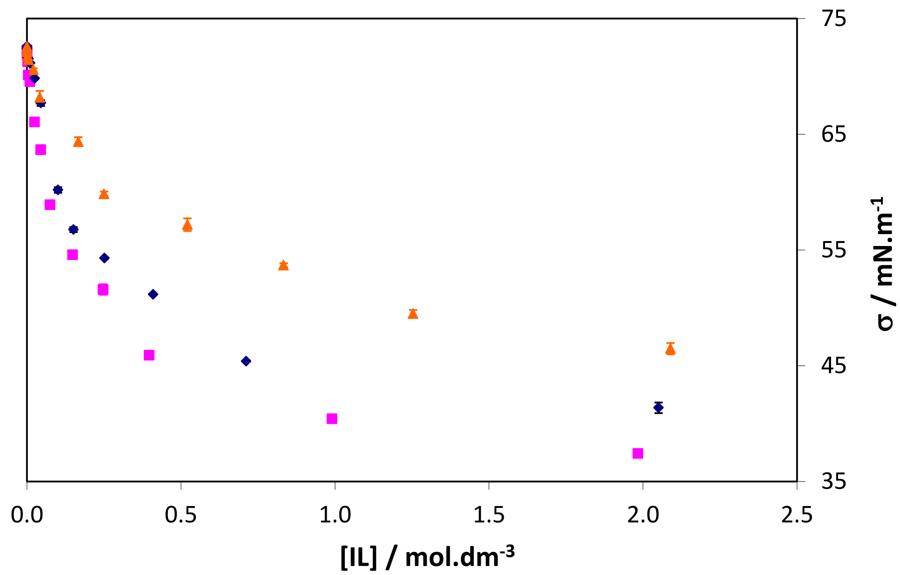


Figure S2. .Surface tension values at 298 K for ▲ $[C_2C_1im]Cl$, ◷ $[C_4C_1im]Cl$, **○** $[C_6C_1im]Cl$ in logarithmic scale and linear scale.

Experimental part

Surface tension: The surface tension of the ILs was measured with a NIMA DST 9005 tensiometer from NIMA Technology, Ltd., equipped with a precision balance able to measure down to 10^{-9} N, using the Pt/Ir Du Noüy ring at atmospheric pressure. The sample surface was cleaned before each measurement by aspiration to remove the surface active impurities present at the interface and to allow the formation of a new interface. The measurements were carried at 298 K and at atmospheric pressure. The sample under measurement was kept thermostatized in a double-jacketed glass cell by means of a water bath, using an HAAKE F6 circulator equipped with a Pt100 probe immersed in the solution and able to control the temperature within (0.01 K).

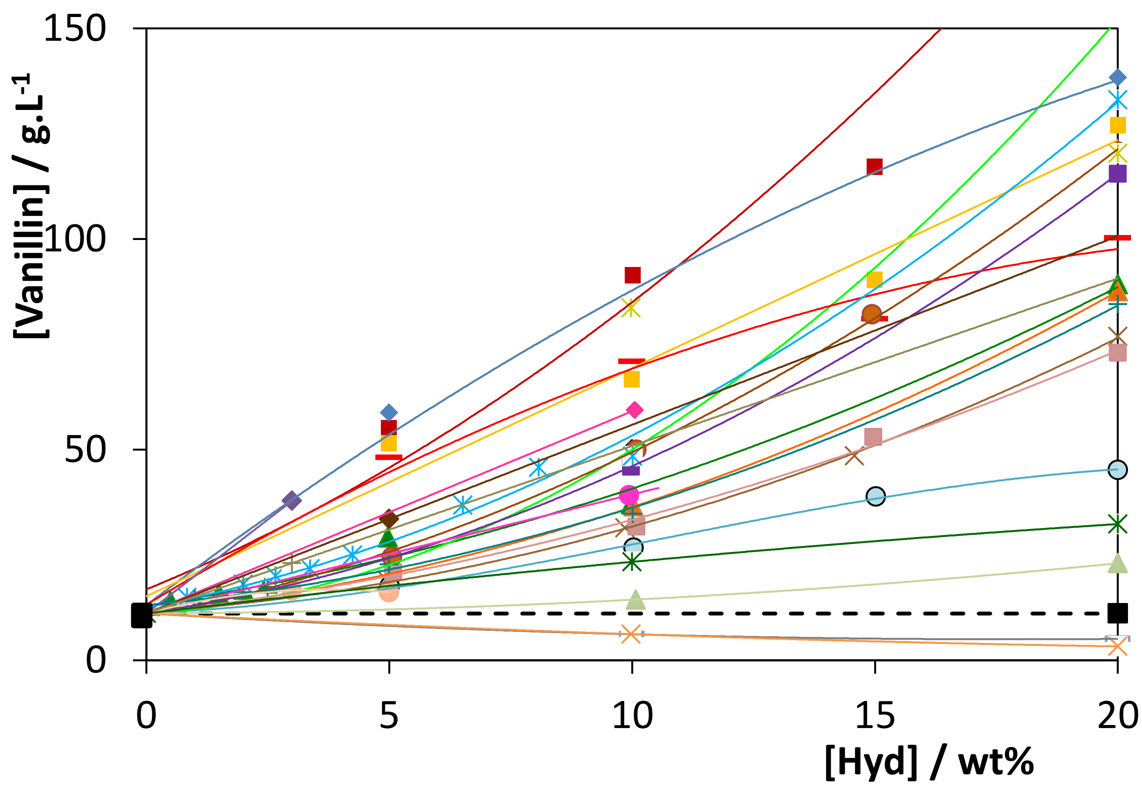


Figure S3. Influence of the hydrotropes (ionic liquids and conventional salts) concentration in the solubility of vanillin in aqueous solutions at 303 K: (---,O) pure water, ( ) [C_2C_1im]Cl, (□) [C_4C_1im]Cl, (◆) [C_6C_1im]Cl, (O) [C_8C_1im]Cl, (◆) [$C_{10}C_1$im]Cl, (O) [$C_{12}C_1$im]Cl, (—) [$C_{14}C_1$im]Cl, ( ) [C_2C_1im][N(CN)$_2$], (◆) [C_4C_1im][N(CN)$_2$], (◆) [C_4C_1py][N(CN)$_2$], (O) [C_4C_1py]Cl, (□) [C_4C_1pyrr]Cl, ( ) [C_4C_1pip]Cl, ( ) [C_4C_1im][TOS], ( ) [C_4C_1im][SCN], (O) Na[$C_7H_5O_2$], (□) Na[SCN], (—) Na[$C_6H_5O_7$], ( ) NaCl, ( ) [N_{4444}]Cl, (+) Na[TOS], (◆) [P_{4444}]Cl, ( ) [N_{4444}][TOS], (+) [P_{4441}][TOS], and ( ) Na[N(CN)$_2$]. Lines are guides for the eye.

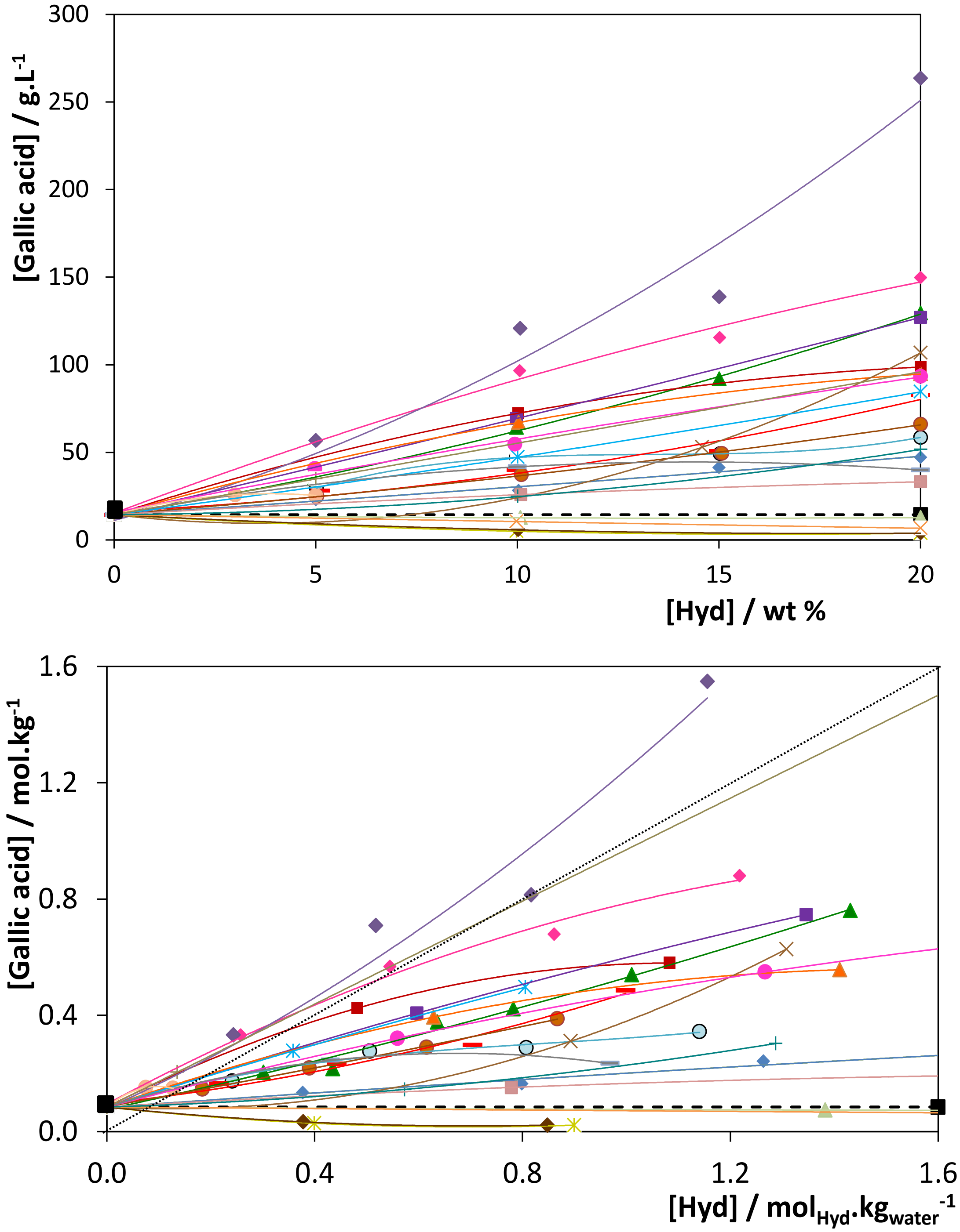


Figure S4. Influence of the hydrotropes (ionic liquids and conventional salts) concentration in the solubility of vanillin in aqueous solutions at 303 K: (---,**O**) pure water, [C_4C_1im]Br, [C_4C_1im]Cl, [C_8C_1im]Cl, [N_{1112}(OH)] Cl, [C_4C_1im][CH_3SO_3], [C_2C_1im] [N(CN)$_2$], [C_4C_1im] [N(CN)$_2$], [C_4C_1py][N(CN)$_2$], [C_4C_1py]Cl, [C_4C_1pyrr]Cl, [C_4C_1pip]Cl, [C_4C_1im][TOS], [C_4C_1im][SCN], Na[$C_7H_5O_2$], Na[SCN], Na[$C_6H_5O_7$], NaCl, [N_{4444}]Cl, + Na[TOS], [P_{4444}]Cl, [N_{4444}][TOS], + [P_{4441}][TOS].

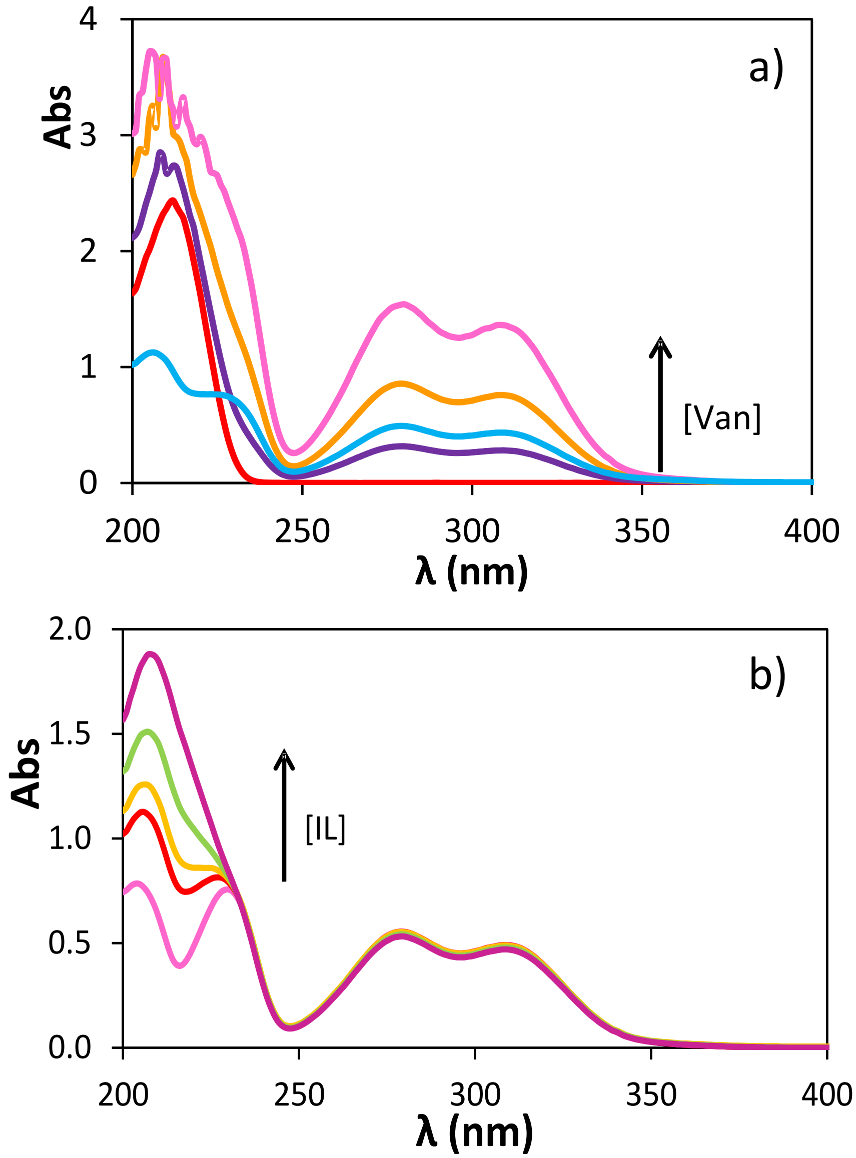


Figure S5. UV spectra of a) aqueous solution of $[C_4C_1im]Cl$ with addition of vanillin; b) aqueous solution of vanillin with adittion of $[C_4C_1im]Cl$

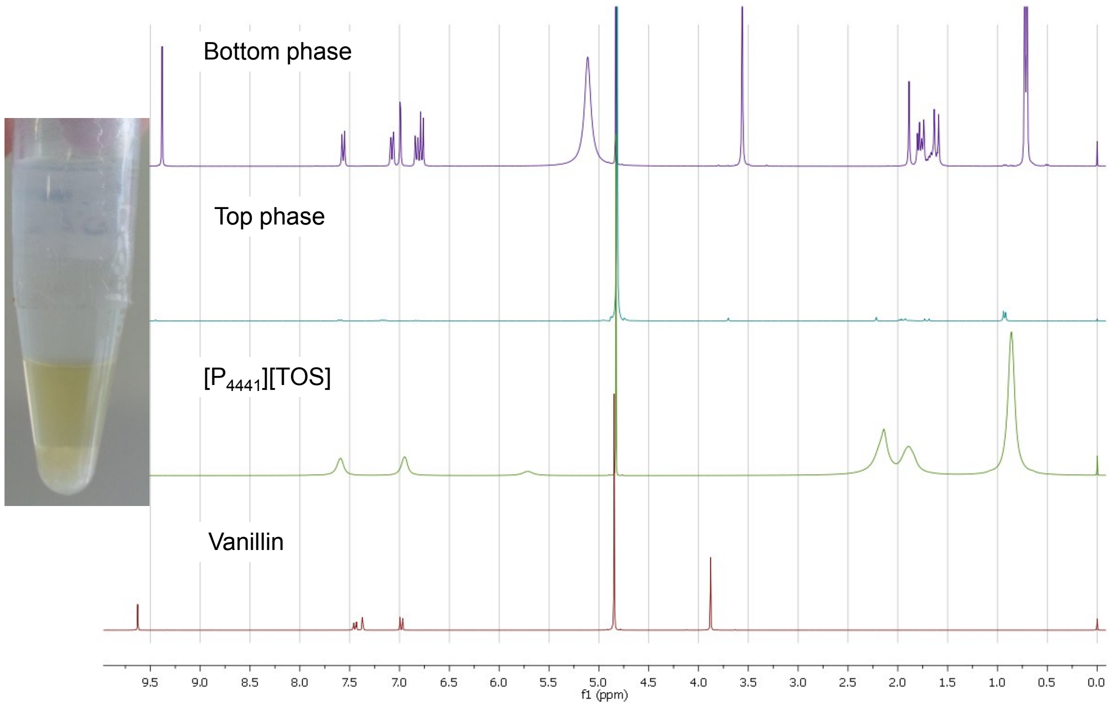


Figure S6. [1]H NMR of pure $[P_{4441}][TOS]$, pure vanillin, and top and bottom phases of the system composed of vanillin and an aqueous solution of $[P_{4441}][TOS]$.

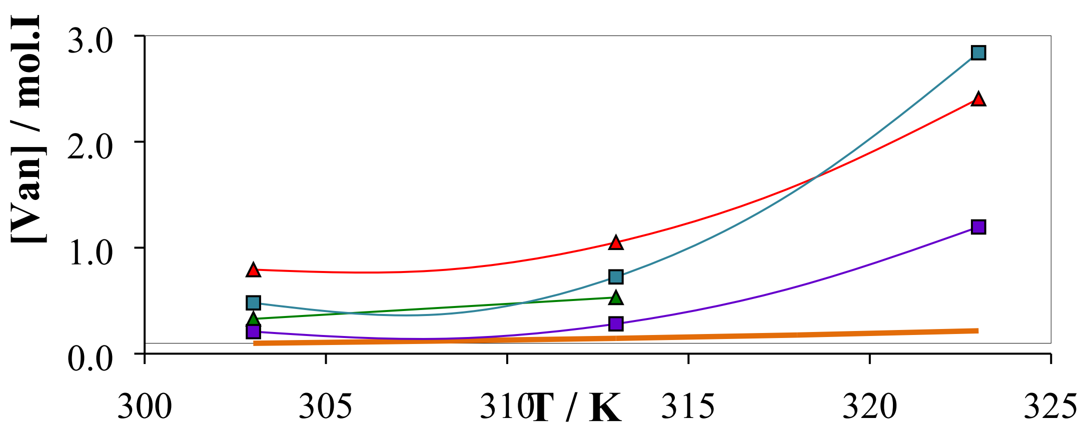


Figure S7. Influence of temperature in the vanillin's solubility in — water and in aqueous solutions of ○ 10 wt % of sodium benzoate (0.70 mol.L^{-1}), □ 10 wt % of $[C_2C_1im][N(CN)_2]$ (0.57 mol.L^{-1}), ○ 20 wt % of sodium benzoate (1.39 mol.L^{-1}), and □ 20 wt % of $[C_2C_1im][N(CN)_2]$ (1.13 mol.L^{-1}).

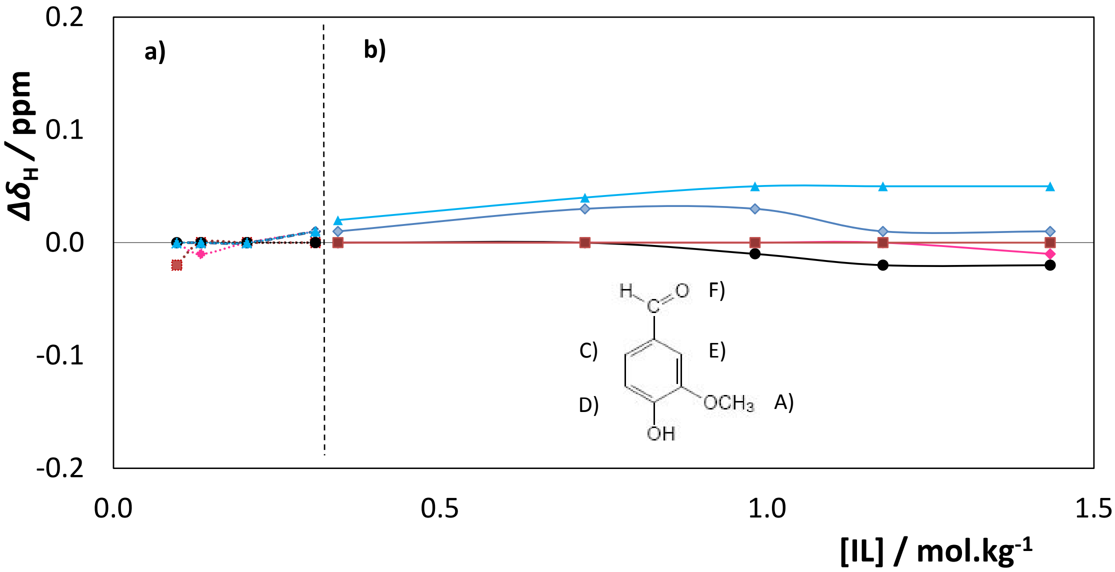


Figure S8. [1]H-NMR chemical shift deviations of **a)** [Vanillin] (0.05 mol·kg^{-1}); **b)** [Vanillin] (0.13 mol·kg^{-1}) as a function of the IL molality: ● A, ◆ C, ◆ D, ○ E, □ F.