SUPPLEMENTARY INFORMATION

Assessing the hydrotropic effect in the presence of electrolytes: competition between solute salting-out and salt-induced hydrotrope aggregation

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TABLES

Table S1. Aqueous vanillin solubility as a function of the concentration (solute-free basis) of [C_4mim]Cl in the absence of additional inorganic salts (T = 303.2 K). The he aqueous vanillin solubility of 13.1 g.L^{-1} at 303.2 K was taken from Abranches et al [1].

	LiCl	
[LiCl] (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.00	13.10	-
0.20	12.42	0.22
0.40	11.56	0.10
0.50	11.12	0.78
1.00	8.83	0.10
2.00	5.99	0.10
3.00	4.62	0.16
4.00	3.63	0.52
5.00	3.60	0.04
	NaCl	
[NaCl] (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.00	13.10	-
0.50	10.25	0.18
1.00	7.96	0.32
2.00	5.29	0.33
3.00	3.81	0.24
4.00	3.28	0.04
	$CaCl_2$	
[$CaCl_2$] (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.00	13.10	-
0.50	9.81	0.37
1.00	7.19	0.29
2.00	4.81	0.58
3.00	3.25	0.27
4.00	2.86	0.37
	YCl_3	

$[YCl_3]$ (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.00	13.10	-
0.30	10.10	0.23
0.60	8.11	0.11
0.90	7.11	0.18
1.20	6.44	0.29
1.50	5.79	0.11

Table S2. Aqueous vanillin solubility for a starting $[C_4mim]Cl$ concentrations of 0.5 mol.kg^{-1} in the presence of individual salts (T = 303.2 K).

	LiCl	
[LiCl] (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.000	43.23	-
0.502	38.02	2.08
1.060	33.17	2.49
1.960	25.21	0.67
4.050	17.76	0.35
6.030	15.20	0.37
6.950	13.78	0.19
7.930	15.08	0.12
8.940	12.85	0.16
	NaCl	
[NaCl] (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.000	43.23	
0.482	35.47	0.44
1.017	30.19	1.11
1.490	28.93	0.61
1.985	26.15	0.89
2.451	24.42	0.51
2.978	23.44	0.48
3.320	21.01	0.21
	KCl	
[KCl] (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.000	43.23	
0.496	40.76	2.26
1.000	39.03	0.32
1.521	33.11	0.25
2.006	32.18	0.08
2.623	28.35	0.54
	$CaCl_2$	

$[CaCl_2]$ ($mol.kg^{-1}$)	[Vanillin] ($g.L^{-1}$)	± σ
0.000	43.23	
0.537	35.33	0.44
1.075	27.62	0.84
1.613	19.92	0.46
2.135	19.67	0.15
2.700	19.27	0.76

YCl_3

$[YCl_3]$ ($mol.kg^{-1}$)	[Vanillin] ($g.L^{-1}$)	± σ
0.000	43.23	
0.506	30.04	1.11
1.015	21.33	0.45
1.504	18.17	0.42

Table S3. Aqueous vanillin solubility for a starting $[C_4mim]Cl$ concentrations of 1.5 mol.kg^{-1} in the presence of individual salts (T = 303.2 K).

LiCl		
[LiCl] (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.000	279.77	
0.513	227.63	6.93
1.120	157.53	7.93
2.000	137.35	5.78
3.020	105.54	10.29
4.010	93.28	9.60
4.980	94.40	6.96
5.990	85.50	2.69
6.420	81.12	1.54
NaCl		
[NaCl] (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.000	279.77	
0.493	229.07	0.92
1.019	207.59	8.13
1.503	202.97	2.81
1.994	192.38	2.41
2.501	211.32	1.50
KCl		
[KCl] (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.000	279.77	
0.502	200.68	17.48
1.012	214.90	1.48
1.406	209.08	5.91
1.577	209.78	2.96
$CaCl_2$		
[$CaCl_2$] (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.000	279.77	
0.489	145.55	10.91

0.996	126.31	2.70
1.424	107.57	3.45
1.697	100.81	4.88

YCl_3

[YCl_3] (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.000	279.77	
0.484	147.57	0.74

Table S4. Aqueous vanillin solubility as a function of the concentration (solute-free basis) of inorganic chloride salts (T = 303.2 K).

LiCl		
[LiCl] (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.00	13.10	0.22
0.20	12.42	0.10
0.40	11.56	0.78
0.50	11.12	0.10
1.00	8.83	0.10
2.00	5.99	0.16
3.00	4.62	0.52
4.00	3.63	0.04
5.00	3.60	0.02
NaCl		
[NaCl] (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.00	13.10	0.22
0.50	10.25	0.18
1.00	7.96	0.32
2.00	5.29	0.33
3.00	3.81	0.24
4.00	3.28	0.04
$CaCl_2$		
[$CaCl_2$] (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.00	13.10	0.22
0.50	9.81	0.37
1.00	7.19	0.29
2.00	4.81	0.58
3.00	3.25	0.27
4.00	2.86	0.37
YCl_3		
[YCl_3] (mol.kg^{-1})	**[Vanillin] (g.L^{-1})**	**± σ**
0.00	13.10	0.22

0.30	10.10	0.23
0.60	8.11	0.11
0.90	7.11	0.18
1.20	6.44	0.29
1.50	5.79	0.11

Table S5. δ_H of the $[C_4mim]^+$ cationic hydrogens in the various studied systems. A constant IL and salt concentrations of 1.5 mol.kg^{-1} and 1.0 mol.kg^{-1} were used respectively and vanillin was added to saturation in the indicated systems. Peak labelling corresponds to that in **Figure 3** of the manuscript or **Figure S1** of the ESI.

System	Peak label							
	8	7	6	5	4	3	2	1
$[C_4mim]Cl$	4.04	7.34	7.29	8.60	3.74	1.67	1.15	0.73
$[C_4mim]Cl$ + LiCl	3.99	7.32	7.27	8.59	3.70	1.61	1.08	0.66
$[C_4mim]Cl$ + NaCl	3.96	7.3	7.25	8.57	3.67	1.57	1.04	0.62
$[C_4mim]Cl$ + $CaCl_2$	3.90	7.25	7.2	8.52	3.62	1.54	0.97	0.55
$[C_4mim]Cl$ + YCl_3	3.75	7.13	7.09	8.41	3.48	1.33	0.78	0.36
$[C_4mim]Cl$ + vanillin	3.82	7.19	7.18	8.49	3.45	1.40	0.92	0.48
$[C_4mim]Cl$ + vanillin + NaCl	3.89	7.22	7.20	8.50	3.52	1.51	1.01	0.60
$[C_4mim]Cl$ + vanillin + $CaCl_2$	3.76	7.14	7.12	8.44	3.38	1.33	0.82	0.40
$[C_4mim]Cl$ + vanillin + YCl_3	3.67	7.07	7.06	8.37	3.30	1.23	0.67	0.27

Table S6. δ_H of the vanillin hydrogens in the various studied systems. A constant IL and salt concentrations of 1.5 mol.kg^{-1} and 1.0 mol.kg^{-1} were used respectively and vanillin was added to saturation. Peak labelling corresponds to that in **Figure 3** of the manuscript.

System	Peak label				
	5	4	3	2	1
Vanillin	9.48	7.21	7.31	6.85	3.73
$[C_4mim]Cl$ + vanillin	9.21	6.80	6.95	6.57	3.63
$[C_4mim]Cl$ + vanillin + NaCl	9.27	6.87	7.02	6.61	3.68
$[C_4mim]Cl$ + vanillin + $CaCl_2$	9.15	6.73	6.88	6.52	3.58
$[C_4mim]Cl$ + vanillin + YCl_3	9.12	6.71	6.84	6.45	3.48

FIGURES

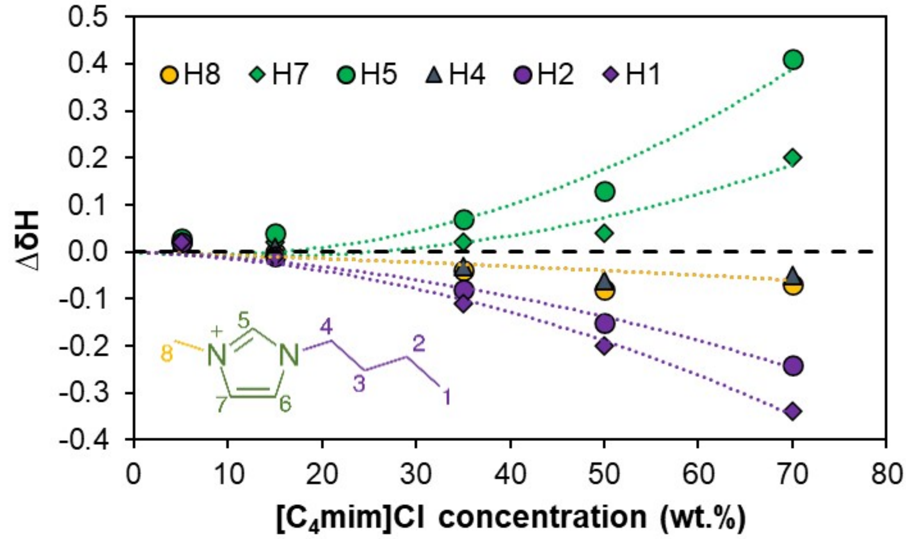

Figure S1. Proton chemical shifts ($\Delta\delta_H$) of the $[C_4mim]^+$ cation as a function of its aqueous concentration relative to a 2.0 wt.% IL solution.

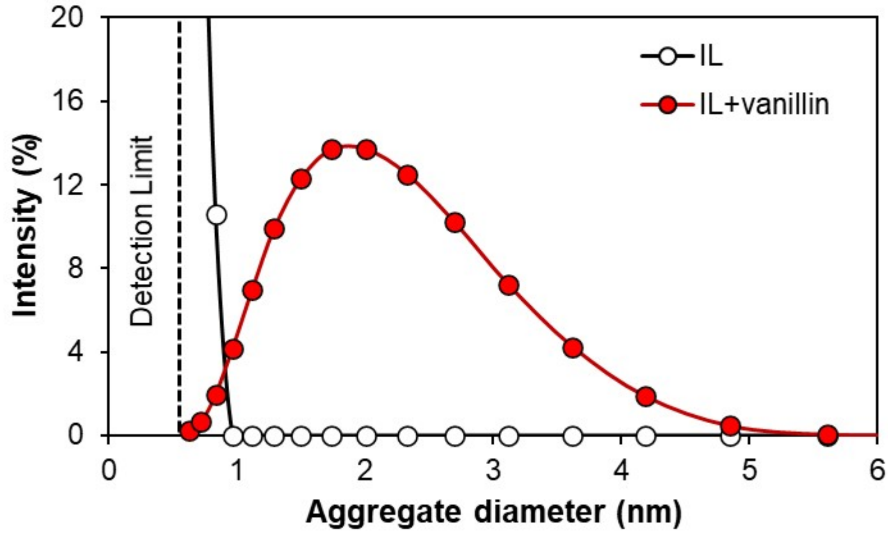

Figure S2. Aggregate size distribution by intensity obtained by DLS in an 1.5 M $[C_4mim]Cl$ aqueous solution and the same solution saturated with vanillin (T = 298 K).

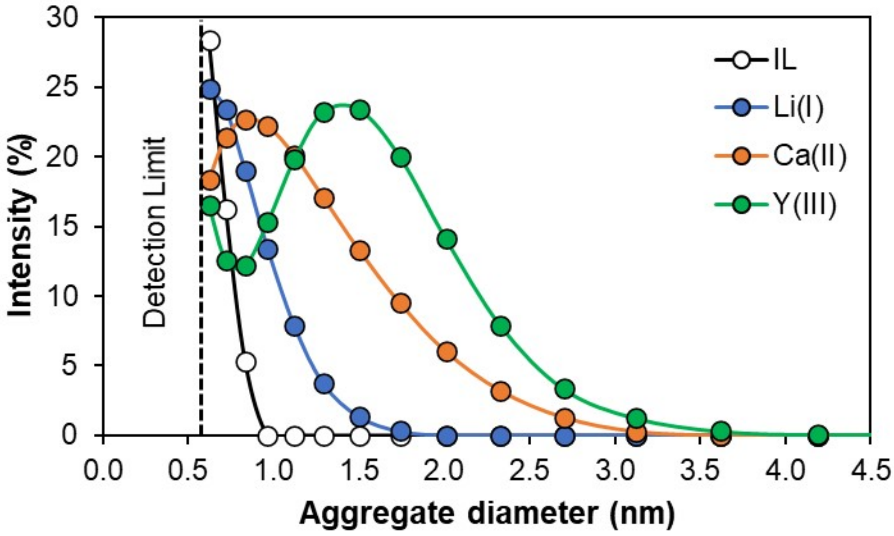

Figure S3. Aggregate size distribution by intensity obtained by DLS in 1.5 mol.kg^{-1} [C_4mim]Cl aqueous solutions with 1.0 mol.kg^{-1} of inorganic chloride salts and no vanillin.

REFERENCE

[1] D. O. Abranches, J. Benfica, B. P. Soares, A. M. Ferreira, T. E. Sintra, S. Shimizu and J. A. P. Coutinho, The impact of the counterion in the performance of ionic hydrotropes. *Chem. Commun.*, 2021, **57**, 2951–2954.