Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Exploring the impact of sodium salts on the hydrotropic solubilization

Jordana Benfica,[a] Afonso C. Martins,[a] Germán Peréz-Sanchéz,[a] Nicolas Schaeffer,[a*] João A. P. Coutinho[a*]

[a] CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.

* Corresponding E-mail: nicolas.schaeffer@ua.pt | jcoutinho@ua.pt

TABLES

Table S1. Solubility of syringic acid in mixture of 1.0 mol L^{-1} of $[C_4mim]Cl$ with 1.0 mol L^{-1} of sodium salts at T = 303.2 K.

Compounds	Concentration (mol L^{-1})	Solubility (g L^{-1})
Water	Pure	1.48 ± 0.07
$[C_4mim]Cl$	1.0	18.08 ± 0.21
$[C_4min]Cl + N_2[SO_4]$	1.0	11.43 ± 0.37
$[C_4min]Cl + Na[Cl]$	1.0	16.96 ± 1.05
$[C_4min]Cl + Na[NO_3]$	1.0	17.31 ± 0.29
$[C_4min]Cl + Na[SCN]$	1.0	19.38 ± 0.33
$[C_4min]Cl + Na[TOs]$	1.0	40.03 ± 0.15
$[C_4min]Cl+ Na[N(CN)_2]$	1.0	43.32 ± 1.98

Table S2. Aqueous syringic acid solubility in $[C_4mim]Cl$ at T = 303.2 K.

Compounds	Concentration (mol L^{-1})	Solubility (g L^{-1})	± σ (g L^{-1})
$[C_4mim]Cl$	0.00	1.48	0.07
	0.06	1.95	0.28
	0.11	2.35	0.43
	0.17	2.53	0.13
	0.23	2.99	0.41
	0.28	3.68	0.54
	0.57	6.13	0.12
	1.15	18.08	0.21
	1.68	32.18	0.45
	2.26	56.13	0.32
	2.86	92.00	0.46
	3.45	120.28	0.61
	4.01	50.60	0.31

Table S3. Aqueous syringic acid solubility in o $[C_4mim]Cl$ the presence of individual salt Na[N(CN)2] at 0.5, 1.0, 2.0 mol L^{-1} and $[C_4mim][N(CN)_2]$ and at T = 303.2 K.

Compounds	Concentration (mol L^{-1})	Solubility (g L^{-1})	± σ (g L^{-1})
$[C_4mim][N(CN)_2]$	0.00	1.48	0.07
	0.05	4.02	0.51
	0.10	5.31	0.05
	0.15	6.96	0.67
	0.19	8.95	0.72
	0.24	15.67	0.06
	0.49	21.12	0.03
	0.98	31.6	0.30
	1.47	42.28	0.16
	1.95	53.88	0.27
	2.44	51.51	0.23
	2.90	43.43	0.11
	3.41	37.65	0.31
	3.90	31.14	0.34
$[C_4min][Cl]$ + $Na[N(CN)_2]$ 0.5M	0.00	3.87	0.10
	0.58	15.41	0.10
	1.17	26.53	0.25
	1.72	46.03	0.20
	2.30	70.71	2.86
	2.86	101.79	4.15
	3.46	137.03	1.43
	3.98	76.22	1.80
$[C_4min][Cl]$ + $Na[N(CN)_2]$ 1M	0.00	7.50	0.20
	0.57	25.82	0.30
	1.15	45.52	0.10
	1.72	73.59	2.89
	2.29	100.67	3.34
	2.86	132.54	3.33
	3.44	140.18	2.70
	4.01	78.59	1.23
$[C_4min][Cl]$ + $Na[N(CN)_2]$ 2M	0.00	12.63	0.10
	0.60	35.96	0.35
	1.18	59.27	1.43
	1.72	87.33	0.48
	2.32	112.76	0.78
	2.90	138.54	0.56
	3.47	144.67	1.75
	4.03	79.83	1.45

Table S4. Aqueous syringic acid solubility in o $[C_4mim]Cl$ the presence of individual salt Na[SCN] at 0.5, 1.0, 2.0 mol L^{-1} and $[C_4mim][SCN]$ and at T = 303.2 K.

Compounds	Concentration (mol L^{-1})	Solubility (g L^{-1})	± σ (g L^{-1})
$[C_4mim][SCN]$	0.00	1.48	0.07
	0.05	2.10	0.38
	0.10	2.87	0.31
	0.15	3.34	0.33
	0.20	4.97	0.21
	0.25	6.65	0.24
	0.50	7.38	0.09
	1.02	21.41	0.24
	1.50	46.64	0.12
	2.03	72.73	0.11
	2.54	82.60	0.70
	3.04	100.63	0.87
	3.55	118.54	1.37
	4.07	115.34	6.28
$[C_4min][Cl]$ + Na[SCN] 0.5M	0.00	1.82	0.01
	0.58	8.31	0.08
	1.17	17.31	0.18
	1.72	31.48	0.21
	2.30	51.51	1.39
	2.86	75.29	0.87
	3.46	115.89	1.87
	3.98	55.67	2.98
$[C_4min][Cl]$ + Na[SCN] 1M	0.00	2.14	0.02
	0.57	8.89	0.02
	1.15	19.38	0.33
	1.72	33.26	0.22
	2.29	52.90	0.48
	2.86	75.81	1.56
	3.44	103.59	1.11
	4.01	46.62	0.14
$[C_4min][Cl]$ + Na[SCN] 2M	0.00	2.42	0.01
	0.60	9.65	0.02
	1.18	20.91	0.03
	1.72	34.84	0.09
	2.32	55.24	0.86
	2.90	75.42	0.73
	3.47	86.64	1.25
	4.03	53.62	1.13

Table S5. Proton chemical shifts (ΔδH) of the IL cation in a 1.0 mol L^{-1} solution of IL $[C_4mim]^+$ cationic hydrogens in the various studied systems.

Systems	Alkyl				Methyl	Ring		
	1	2	3	4	5	6	7	8
$[C_4mim]Cl$	0.73	1.15	1.67	3.79	4.04	7.29	7.34	8.60
$[C_4mim]Cl + Na[N(CN)_2]$ 0.5M	0.73	1.15	1.68	3.79	4.04	7.29	7.34	8.61
$[C_4mim]Cl + Na[N(CN)_2]$ 1M	0.73	1.15	1.67	3.79	4.04	7.29	7.34	8.61
$[C_4mim]Cl + Na[N(CN)_2]$ 2M	0.73	1.15	1.68	3.78	4.04	7.29	7.34	8.60
$[C_4mim]Cl$ + Na[SCN] 0.5M	0.73	1.15	1.67	3.79	4.04	7.29	7.34	8.60
$[C_4mim]Cl$ + Na[SCN] 1M	0.74	1.15	1.68	3.78	4.04	7.39	7.34	8.60
$[C_4mim]Cl$ + Na[SCN] 2M	0.74	1.15	1.68	3.79	4.04	7.39	7.34	8.61
$[C_4mim]Cl$ + Syringic Acid (SA)	0.71	1.12	1.64	3.72	4.01	7.27	7.32	8.57
$[C_4mim]Cl$ + SA + $Na[N(CN)_2]$ 0.5M	0.68	1.06	1.60	3.69	3.96	7.25	7.28	8.53
$[C_4mim]Cl$ + SA + $Na[N(CN)_2]$ 1M	0.67	1.06	1.60	3.69	3.95	7.24	7.27	8.52
$[C_4mim]Cl$ + SA + $Na[N(CN)_2]$ 2M	0.66	1.05	1.59	3.68	3.94	7.24	7.26	8.49
$[C_4mim]Cl$ + SA + Na[SCN] 0.5M	0.69	1.09	1.63	3.72	4.00	7.27	7.31	8.55
$[C_4mim]Cl$ + SA + Na[SCN] 1M	0.66	1.06	1.61	3.71	3.98	7.26	7.30	8.54
$[C_4min]Cl$ + SA + Na[SCN] 2M	0.61	1.02	1.58	3.71	3.96	7.25	7.29	8.53

Table S6. δH of the syringic acid hydrogens in the systems studied.

Systems	Peak Syringic Acid				
	1	2	3	4	5
Syringic Acid in water (SA)	3.73	3.73	4.75	7.09	7.09
$[C_4mim]Cl$ 1M + SA	3.66	3.66	4.70	6.99	6.99
$[C_4mim]Cl$ 1M + SA + $Na[N(CN)_2]$ 0.5M	3.64	3.64	4.70	6.97	6.97
$[C_4mim]Cl$ 1M + SA + $Na[N(CN)_2]$ 1M	3.64	3.64	4.70	6.97	6.97
$[C_4mim]Cl$ 1M + SA + $Na[N(CN)_2]$ 2M	3.63	3.63	4.70	6.96	6.96
$[C_4mim]Cl$ 1M + SA + Na[SCN] 0.5M	3.65	3.65	4.70	6.98	6.98
$[C_4mim]Cl$ 1M + SA + Na[SCN] 1M	3.63	3.63	4.70	6.96	6.96
$[C_4mim]Cl$ 1M + SA + Na[SCN] 2M	3.61	3.61	4.70	6.93	6.93

Table S7. Results of normalization area under the curve for samples used in this work.

Systems	Peak 753	Peak 2046	Peak 2060	Peak 2075
	Area	Area	Peak	Area
Na[SCN] 0.5M	0.1567	0.1400	0.2504	0.5565
Na[SCN] 1M	0.3202	0.2690	0.6025	0.9740
Na[SCN] 2M	0.7009	0.5307	2.8150	1.1235
C_4minCl 0.5M + Na[SCN] 2M	0.4910	0.7390	1.6150	2.3200
C_4minCl 1M + Na[SCN] 2M	0.8098	1.1252	1.0952	2.5048
C_4minCl 2M + Na[SCN] 2M	1.1959	1.6843	2.1722	2.4282
C_4minCl 3M + Na[SCN] 2M	1.3794	1.7219	3.5755	1.9503
C_4minCl 3.5M + Na[SCN] 2M	1.3964	1.7337	3.9688	1.2997

FIGURES

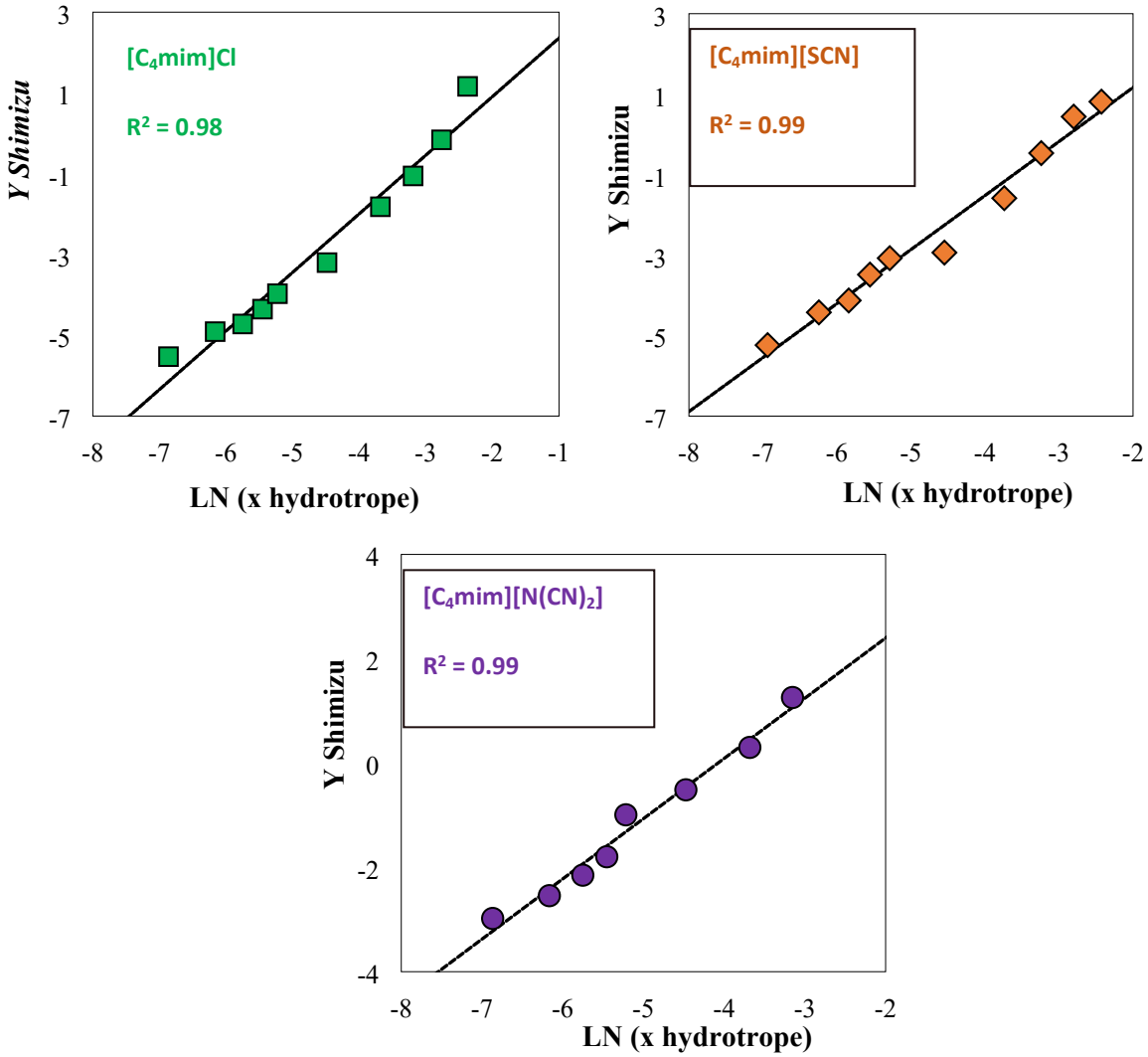

Figure S1. Linearized plot of the cooperative hydrotropy model for the ternary IL + Syringic acid + H_2O systems presented in Figure 2 of the manuscript and calculated based on Eq. 5 (experimental data; dashed line, least-squares fit).

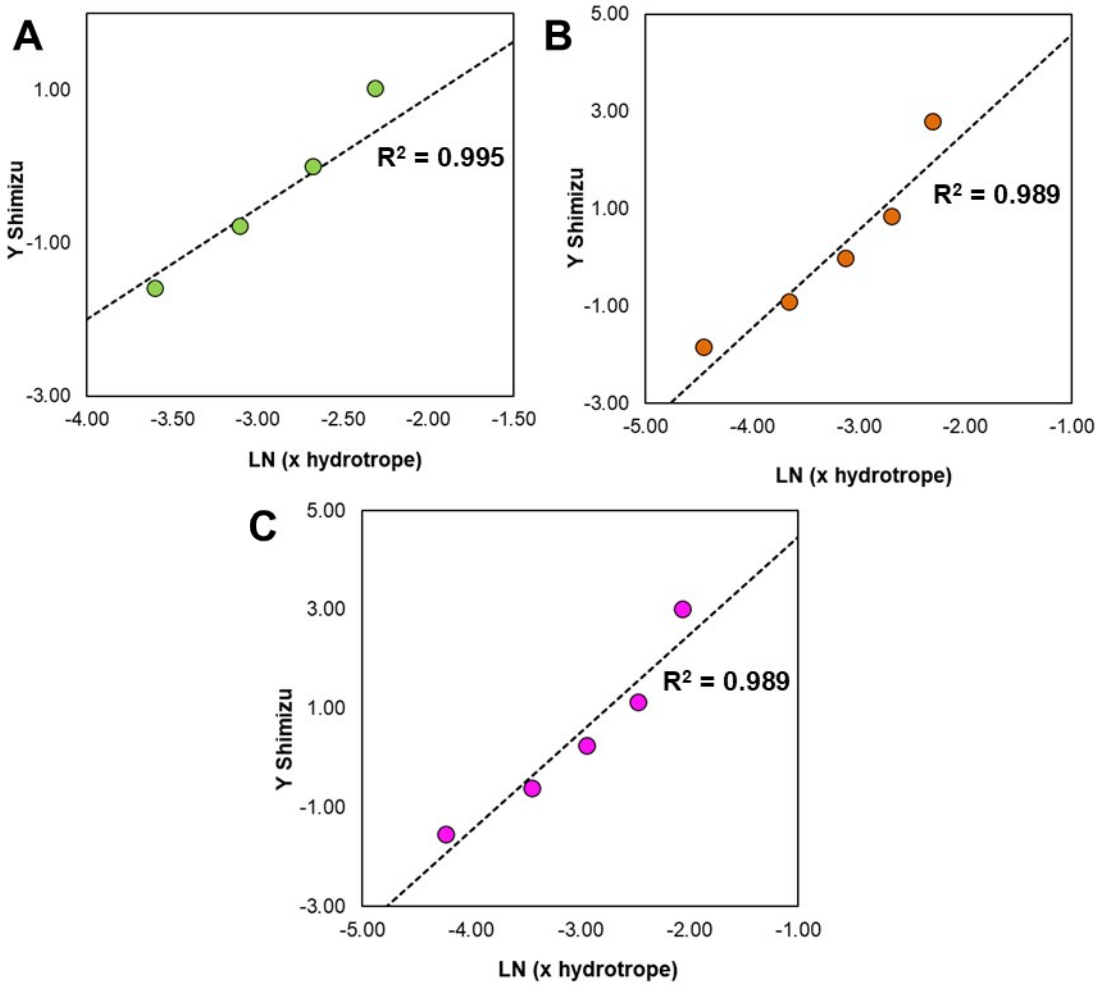

Figure S2. Linearized plot of the cooperative hydrotropy model based on Eq 5 by A) $[C_4mim]Cl + Na[N(CN)_2]$ 0.5 mol L^{-1}; B) $[C_4mim]Cl + Na[N(CN)_2]$ 1.0 mol L^{-1}; and C) $[C_4mim]Cl + Na[N(CN)_2]$ 2.0 mol L^{-1} (experimental data; dashed line, least-squares fit).

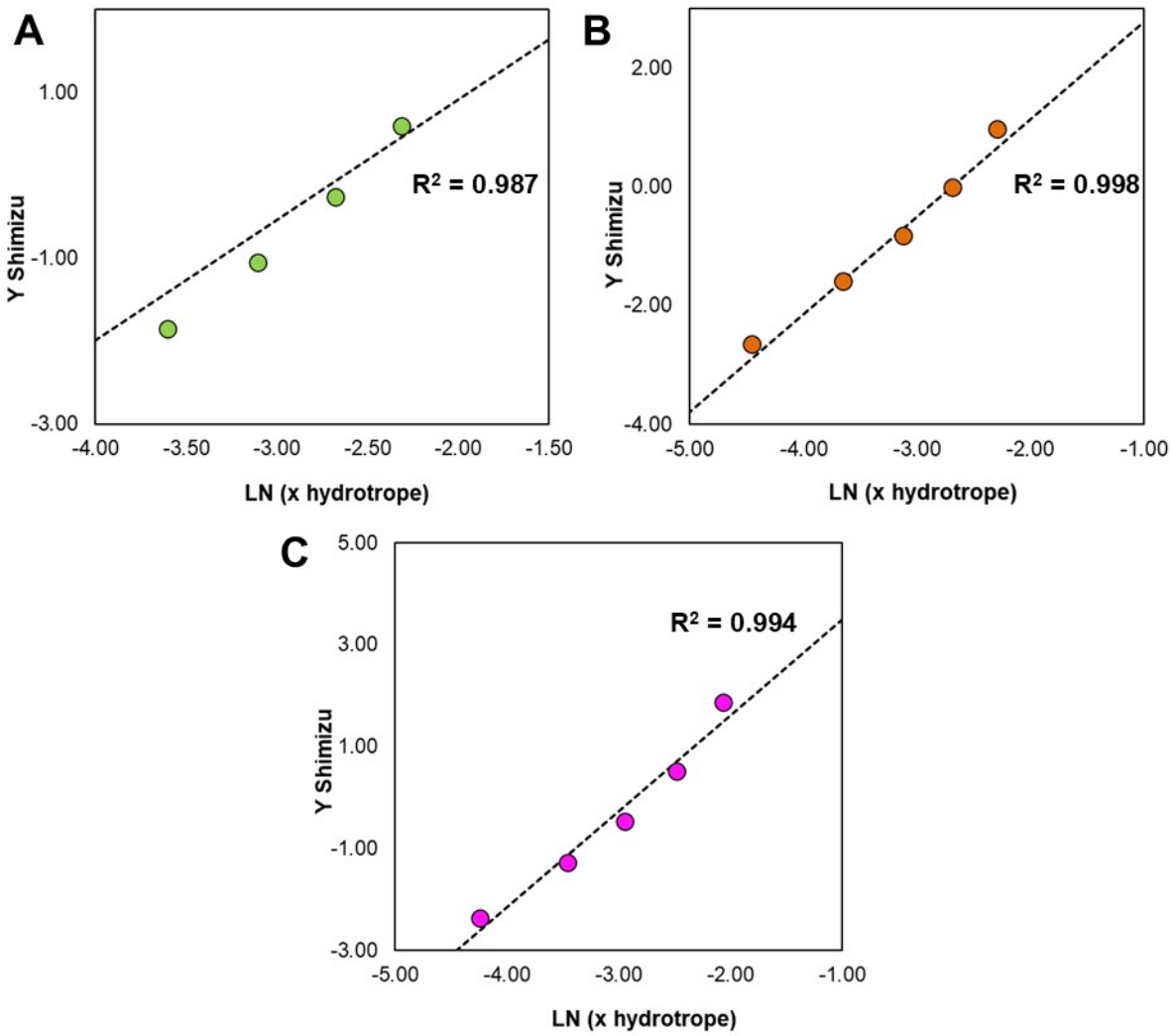

Figure S3. Linearized plot of the cooperative hydrotropy model based on Eq 5 by A) $[C_4mim]Cl$ + Na[SCN] 0.5 mol L^{-1}; B) $[C_4mim]Cl$ + Na[SCN] 1.0 mol L^{-1}; and C) $[C_4mim]Cl$ + Na[SCN] 2.0 mol L^{-1} (experimental data; dashed line, least-squares fit).

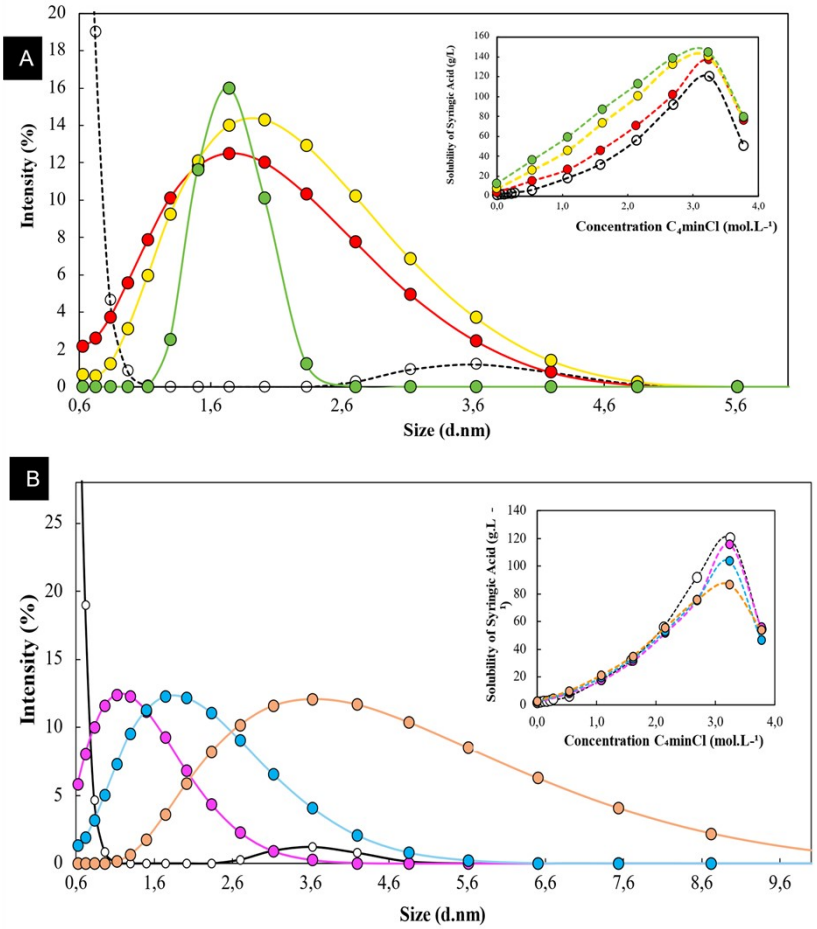

Figure S4. A) Aggregate size distribution by intensity obtained by DLS in (●) 1.0 mol L^{-1} $[C_4mim]Cl$ aqueous solutions saturated with syringic acid and doped with (●) 0.5 mol L^{-1}, (●) 1.0 mol L^{-1} and (●) 2.0 mol L^{-1} of $Na[N(CN)_2]$. **B)** Aggregate size distribution by intensity obtained by DLS in (●) 1.0 mol L^{-1} $[C_4mim]Cl$ aqueous solutions saturated with syringic acid and doped with (●) 0.5 mol L^{-1}, (●) 1.0 mol L^{-1} and (●) 2.0 mol L^{-1} of Na[SCN].