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ELECTRONIC SUPPLEMENTARY INFORMATION

The effect of the cation alkyl chain branching on the behaviour of ionic liquids: Mutual solubilities with water and toxicities

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Table S1 Solubilities of water in the IL-rich phase (x_w) and of IL in the water-rich phase (x_{IL}), expressed in mole fractions, at temperatures from 288.15 to 318.15 K.[a]

	[*i*-C_4C_1im][NTf_2]	[*i*-C_4-3-C_1py][NTf_2]	[*i*-C_4C_1pyrr][NTf_2]	[*i*-C_4C_1pip][NTf_2]	[C_4C_1pip][NTf_2]
T/K			x_w		
288.15	0.216(9)	0.180(8)	0.135(4)	0.117(1)	0.158(1)
293.15	0.224(4)	0.196(3)	0.155(1)	0.134(1)	0.171(6)
298.15	0.241(9)	0.215(1)	0.178(2)	0.155(4)	0.189(3)
303.15	0.257(2)	0.238(5)	0.195(7)	0.173(8)	0.209(3)
308.15	0.277(1)	0.255(8)	0.214(7)	0.195(1)	0.228(1)
313.15	0.293(2)	0.275(1)	0.236(6)	0.213(7)	0.248(6)
318.15	0.310(6)	0.293(1)	0.254(5)	0.233(8)	0.265(4)
T/K			$10^4 \cdot x_{IL}$		
288.15	3.412(2)	2.564(5)	2.764(6)	2.468(6)	1.825(4)
293.15	3.561(1)	2.690(1)	2.890(2)	2.563(3)	1.992(1)
298.15	3.813(5)	2.838(9)	3.038(9)	2.683(1)	2.070(2)
303.15	4.267(3)	2.957(6)	3.227(7)	2.791(9)	2.304(9)
308.15	4.596(1)	3.137(7)	3.437(7)	2.971(6)	2.294(1)
313.15	4.968(1)	3.275(4)	3.675(2)	3.094(6)	2.385(1)
318.15	5.396(4)	3.395(6)	3.895(7)	3.171(7)	2.527(1)

[a]The values between parentheses represent the standard deviation associated with the last representative digit.

Table S2 Fitted parameters from the correlation of the experimental data with equations 1 and 2.[a]

	[*i*-C_4C_1im][NTf_2]	[*i*-C_4-3-C_1py][NTf_2]	[*i*-C_4C_1pyrr][NTf_2]	[*i*-C_4C_1pip][NTf_2]	[C_4C_1pip][NTf_2]
A	2.42(2)	3.51(6)	4.68(6)	5.23(9)	3.79(3)
-*B*/K	1143(41)	1505(36)	1919(69)	2122(61)	1625(28)
-C	172(87)	-0.121(29)	146(22)	18(52)	407(260)
D/K	6177(3918)	-1106(1299)	5308(1010)	-259(2362)	17520(11731)
E	25(13)	-1(4)	21(3)	2(8)	60(39)

[a]The values between parentheses represent the standard deviation of each parameter.

Table S3. Standard thermodynamic molar properties of solution of ILs in water at 298.15 K.[a]

	$\Delta_{sol}G_m^0$ /(kJ · mol^{-1})	$\Delta_{sol}H_m^0$ /(kJ · mol^{-1})	$\Delta_{sol}S_m^0$ /(J · K^{-1} · mol^{-1})
[*i*-C_4C_1im][NTf_2]	19.5(0.005)	11.2(1.5)	-28.0(5.0)
[C_4C_1im][NTf_2] [1]	20.1(0.008)	7.1(1.5)	-43.4(5.1)
[*i*-C_4-3-C_1py][NTf_2]	20.2(0.007)	7.3(1.5)	-43.4(5.0)
[C_4-3-C_1py][NTf_2] [2]	21.0(0.005)	5.3(1.5)	-52.7(5.2)
[*i*-C_4C_1pyrr][NTf_2]	20.1(0.006)	8.1(1.5)	-40.2(5.0)
[C_4C_1pyrr][NTf_2] [3]	20.7(0.010)	5.2(1.5)	-51.9(5.1)
[*i*-C_4C_1pip][NTf_2]	20.4(0.009)	6.6(1.5)	-46.1(5.0)
[C_4C_1pip][NTf_2]	21.0(0.009)	2.3(1.5)	-62.8(5.0)

[a]The values between parentheses represent the standard deviation of each parameter.

Table S4 Molar volume of the studied ionic liquids[a]

Ionic Liquids	V_m/cm^3·mol-1
[C4C1im][NTf2]	292.7539
[*i*-C4C1im][NTf2]	291.7637
[C4C1py][NTf2]	304.3470
[*i*-C4C1py][NTf2]	303.1992
[C4C1pyrr][NTf2]	301.3513
[*i*-C4C1pyrr][NTf2]	301.6945
[C4C1Pip][NTf2]	315.6823
[*i*-C4C1Pip][NTf2]	312.3848

[a] Molar volume is equal to molecular weight per density of ILs. The density of ILs was measured using SVM-3000 Anton Paar Stabinger viscometer-densimeter

Table S5 Microtox® EC_{50} values ($mg.L^{-1}$) of the studied ILs after 5, 15 and 30 min of exposure to the luminescent marine bacteria *V. fischeri*, with the respective 95 % confidence limits (in brackets).

	Ionic liquids	**EC_{50} ($mg.L^{-1}$)** (lower limit; upper limit)		
		5 min	**15 min**	**30 min**
Non-aromatic ILs	$[C_4C_1pyrr][NTf_2]$	532.51 (430.35; 634.68)	436.03 (365.94; 506.12)	416.59 (370.34; 462.84)
	$[i\text{-}C_4C_1pyrr][NTf_2]$	442.22 (259.88; 624.56)	384.80 (164.44; 605.15)	350.39 (252.79; 447.99)
	$[C_4C_1pip][NTf_2]$	352.57 (156.74; 548.40)	311.42 (284.85; 337.99)	304.50 (297.19; 311.82)
	$[i\text{-}C_4C_1pip][NTf_2]$	193.17 (164.79; 221.56)	175.67 (158.06; 193.29)	214.88 (159.25; 270.52)
Aromatic ILs	$[C_4C_1im][NTf_2]$	141.99[a] (70.99; 425.96)	141.99[a] (70.99; 141.99)	---
	$[i\text{-}C_4C_1im][NTf_2]$	442.93[a] (223.57; 585.99)	283.81[a] (210.95; 381.88)	---
	$[C_4\text{-}3\text{-}C_1py][NTf_2]$	42.21 (34.76; 49.67)	38.34 (32.12; 44.57)	43.54 (32.60; 54.48)
	$[i\text{-}C_4\text{-}3\text{-}C_1py][NTf_2]$	137.00 (123.27; 150.73)	113.02 (102.41: 123.63)	134.73 (105.62; 163.83)

[a]Data from reference [4]

Table S6 Studied systems and simulation conditions (equilibrated boxes).

	N ion pairs	N H_2O	V_{box}/nm^3	l_{box}/nm
[C_3C_1im][NTf_2]	320	-	139.8	5.19
[C_4C_1im][NTf_2]	300	-	147.2	5.28
[*i*-C_4C_1im][NTf_2]	300	-	140.6	5.20
[C_3C_1im][NTf_2]	300	130	137.4	5.16
[C_4C_1im][NTf_2]	300	130	144.7	5.25
[*i*-C_4C_1im][NTf_2]	300	130	144.7	5.25
[C_3C_1im][NTf_2]	1	600	19.9	2.71
[C_4C_1im][NTf_2]	1	600	19.0	2.67
[*i*-C_4C_1im][NTf_2]	1	600	19.5	2.69

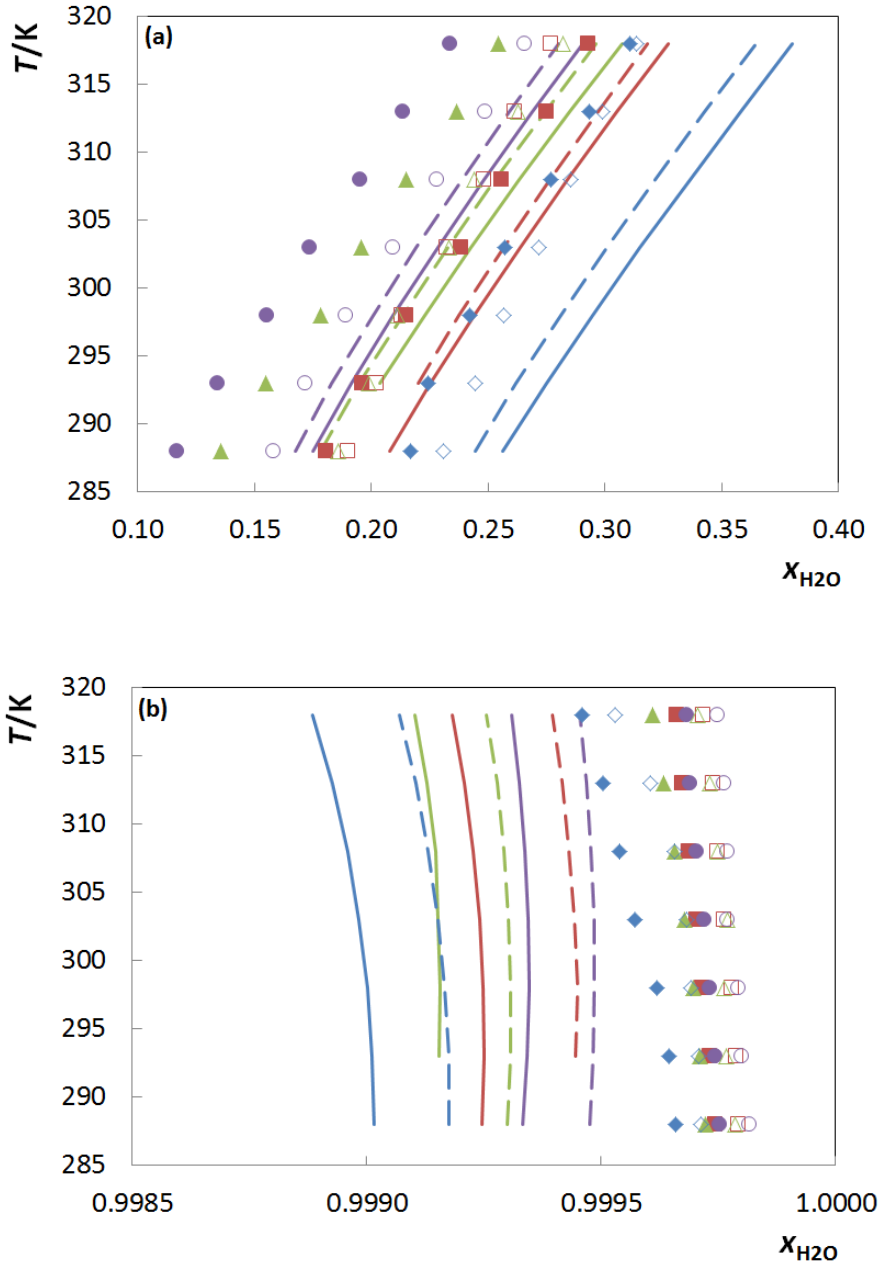
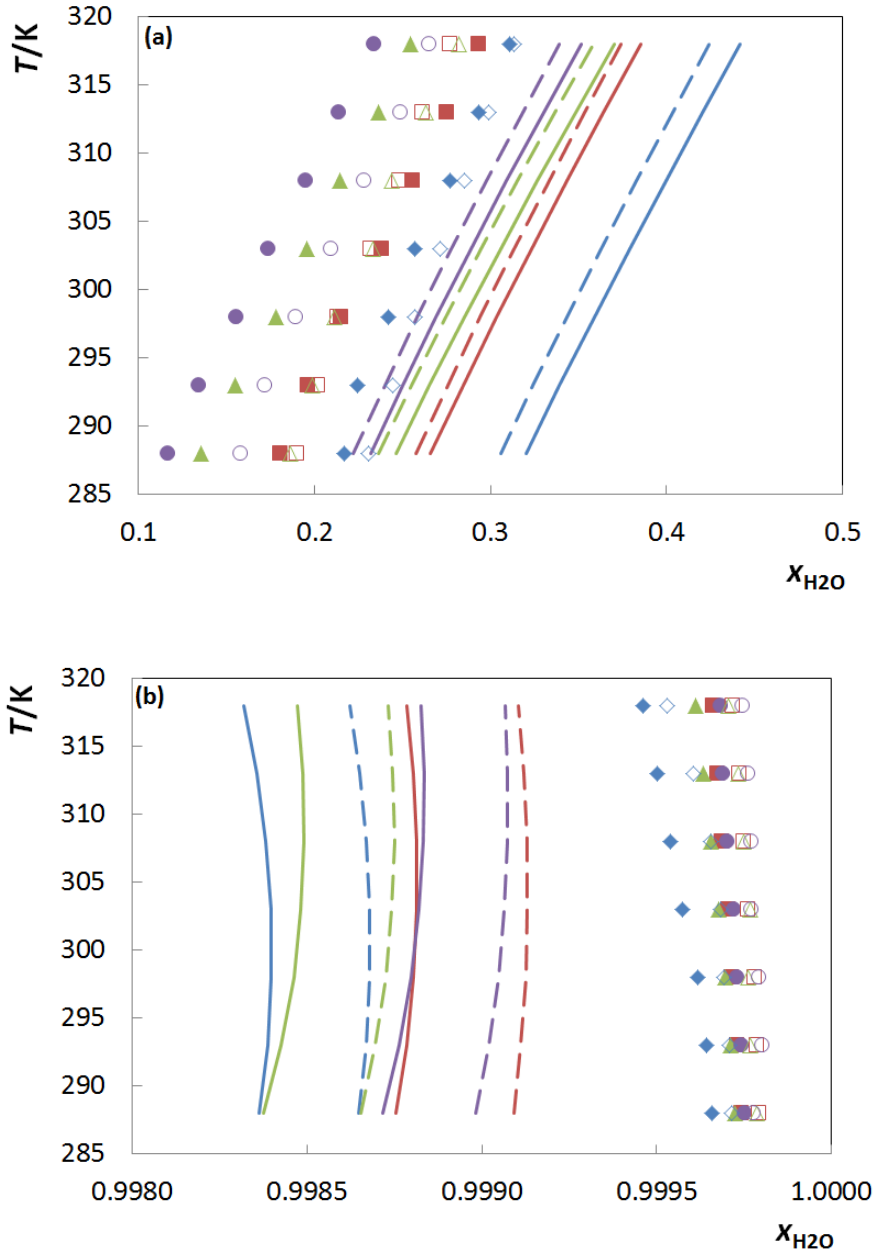


Fig. S1 Liquid-liquid phase diagrams of water and ionic liquids: (a) ionic-liquid-rich phase; and (b) water-rich phase. Symbols (experimental) : (♦,◊) $[C_4C_1im][NTf_2]$; (■,□) $[C_4\text{-}3\text{-}C_1py][NTf_2]$; (▲,Δ) $[C_4C_1pyrr][NTf_2]$; and (●,○) $[C_4C_1pip][NTf_2]$. The closed and open symbols represent *i*-butyl and *n*-butyl, respectively. The matching colour full and dashed lines represent, respectively, the COSMO-RS predictions for the ILs *i*-butyl and *n*-butyl using parameterization BP_TZVP_C20_0111.



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