Zwitterionic compounds are less ecotoxic than their analogous ionic liquids

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Zwitterions physicochemical characterization

Nuclear magnetic resonance. Zwitterions chemical structure was confirmed by ^{1}H nuclear magnetic resonance (NMR) using a Bruker Avance 300 at 300.13 MHz, with deuterium oxide (D_2O) as solvent and trimethylsilyl propanoic acid (TSP) as the internal reference.

Elemental analysis. The elemental analysis was performed by using a TruSpec 630-200-200 elemental analyzer (LECO).

Differential scanning calorimetry. Differential scanning calorimetry (DSC) was performed with a Diamond DSC (PerkinElmer) at a heating rate of 5 °C/min, for the determination of the melting temperature (T_m).

Thermogravimetric analysis. Thermogravimetric analyses (TGA) were performed with a Setsys Evolution 1750, Setaram, TGA mode (S type sensor), at a heating rate of 10 °C/min under nitrogen atmosphere, for the determination of the decomposition temperature (T_d).

N_{444}C3S: δ_H (300 MHz; D_2O; δ/ppm relative to TMS): 0.85 (9H, t), 1.25 (6H, dq), 1.57 (6H, dt), 2.04 (2H, m), 2.86 (2H, t), 3.14 (6H, m), 3.29 (2H, m). Elemental analysis (%) for $C_{15}H_{33}NO_3S$: Found: C, 59.55; H, 10.40; N, 4.60; S, 10.01; C/N, 12.95. Calculated: C, 58.99; H, 10.82; N, 4.56; S, 10.43; C/N, 12.94. T_m: 179 °C. T_d: 276 °C.

N_{222}C3C: δ_H (300 MHz; D_2O; δ/ppm relative to TMS): 1.28 (9H, m), 1.91 (2H, m), 2.27 (2H, t), 3.16 (2H, m), 3.28 (6H, m). Elemental analysis (%) for $C_{10}H_{21}NO_2$: Found: C, 63.82; H, 10.87; N, 7.23; C/N, 8.78. Calculated: C, 64.13; H, 11.3; N, 7.48; C/N, 8.57. T_m: 103 °C. T_d: 172 °C.

C_4ImC3C: δ_H (300 MHz; D_2O; δ/ppm relative to TMS): 0.81 (3H, t), 1.19 (2H, m), 1.73 (2H, m), 2.02 (4H, m), 4.09 (4H, td), 7.39 (2H, dd), 8.88 (1H, s). Elemental analysis (%) for $C_{10}H_{21}NO_2$: Found: C, 62.64; H, 8.66; N, 12.98; C/N, 4.82. Calculated: C, 62.83; H, 8.63; N, 12.32; C/N, 4.71. T_m: 143°C. T_d: 190°C.

C_1ImC5C: δ_H (300 MHz; D_2O; δ/ppm relative to TMS): 1.16 (2H, m), 1.45(2H, m), 1.73 (2H, m), 2.03 (2H, t), 3.75 (3H, s), 4.05 (2H, m), 7.29 (1H, s), 7.34 (1H, d), 9.00 (1H, s). Elemental analysis (%) for $C_{10}H_{21}NO_2$: Found: C, 60.50; H, 7.78; N, 14.27; C/N, 4.24. Calculated: C, 61.2; H, 8.22; N, 14.27; C/N, 4.29. T_m: 120°C. T_d: 243°C.

Table S1. Effective concentration inducing 20 % of effect (EC_{20}), and respective 95% confidence intervals within brackets, of ZIs to the freshwater microalga *R. subcapitata* (96 h of exposure) and the marine bacteria *A. fischeri* (30 min of exposure).

ZIs	***R. subcapitata*** **EC_{20}-96h (g L^{-1})**	***A. fischeri*** **EC_{20}-30min (g L^{-1})**
$N_{555}C3S$	0.07482 (0.04789 - 0.1018)	0.6912 (0.4280 - 0.9543)
$N_{444}C3S$	0.4375 (0.3365 - 0.5384)	2.897 (2.065 - 1.813)
$N_{333}C3S$	2.515 (2.337 - 2.692)	0.5330 (0.5009 - 0.5651)
$N_{222}C4S$	9.767 (7.577 - 11.96)	25.78 (11.15 - 40.40)
$N_{222}C3S$	24.39 (19.63 - 29.15)	0.8714 (0.5327 - 1.210)
$N_{222}C3C$	8.601 (6.218 - 10.98)	66.01 (49.80 - 82.22)
$N_{111}C4S$	26.94 (21.80 - 32.09)	0.6800 (0.5995 - 0.7604)
$N_{111}C3S$	25.44 (20.83 - 30.06)	0.8358 (0.6960 - 0.9756)
C_4ImC3C	6.124 (4.917 - 7.332)	22.431 (19.14 - 25.72)
C_1ImC5C	1.161 (0.804 - 1.518)	6.690 (5.481 - 7.900)
C_1ImC4S	18.42 (16.12 - 20.72)	0.6887 (0.2871 - 1.090)
C_1ImC3C	8.861 (8.078 - 9.643)	2.451 (1.577 - 3.325)
ViImC4S	16.14 (14.06 - 18.21)	1.196 (0.620 - 1.771)
$C_1PyrC4S$	14.06 (10.92 - 17.20)	88.92 (65.65 - 112.2)
PyC4S	12.22 (10.49 - 13.95)	47.18 (33.16 - 61.19)
$C_2PipC4S$	8.435 (7.404 - 9.467)	1.409 (0.179 - 2.640)
Betaine	11.75 (9.000 - 14.50)	89.79 (78.93 - 100.6)

Table S2. Name and acronym of ionic liquids used in this work for comparison proposes, and reported median effective concentration (EC_{50}) values, with the respective 95% confidence intervals (within brackets): *n.a.* - not available.

	Name	Acronym	*R. subcapitata* EC_{50}-96h ($g \cdot L^{-1}$)	*A. fischeri* EC_{50}-30min ($g \cdot L^{-1}$)
i	tetrabutylammonium bromide	$[N_{4444}]Br$	0.722 [1]	0.60 [2]
ii	tetrabutylammonium chloride	$[N_{4444}]Cl$	2.558×10^{-3} (1.992×10^{-3} – 3.124×10^{-3}) [b]	0.1724 (0.1132 – 0.2316) [b]
iii	tetrabutylammonium methanesulfonate	$[N_{4444}][C_1SO_3]$	1.00×10^{-3} (0.89×10^{-3} – 1.12×10^{-3}) [b]	0.2377 (0.2049 – 0.2705) [b]
Iv	tetrapropylammonium chloride	$[N_{3333}]Cl$	*n.a.*	0.5456 (0.4870 – 0.6040) [3]
v	tetraethylammonium chloride	$[N_{2222}]Cl$	*n.a.*	19.24 (13.27 – 25.21) [3]
vi	tetramethylammonium chloride	$[N_{1111}]Cl$	*n.a.*	22.69 (17.48 – 27.90) [3]
vii	cholinium chloride	$[N_{111(2OH)}]Cl$	0.6296 (0.2012 – 1.058) [4]	0.4693 (0.3838 – 0.5549) [5]
viii	cholinium acetate	$[N_{111(2OH)}][C_1CO_2]$	0.8358 (0.7702 – 0.9014) [4]	0.6732 (0.6065 – 0.7399) [5]
ix	1-dodecyl-3-methylimidazolium chloride	$[C_{12}C_1Im]Cl$	2.021×10^{-5} (1.548×10^{-5} – 2.494×10^{-5}) [a 6]	3.736×10^{-4} (3.504×10^{-4} – 3.967×10^{-4}) [6]
x	1-butyl-3-methylimidazolium chloride	$[C_4C_1Im]Cl$	*n.a.*	0.5188 (0.4761 – 0.5764) [7]
xi	1-butyl-3-methylimidazolium bromide	$[C_4C_1Im]Br$	0.229 (0.148 – 0.355) [8]	*n.a.*
xii	1-ethyl-3-methylimidazolium chloride	$[C_2C_1Im]Cl$	0.2652 (0.1617 – 0.3686) [a 6]	6.270 (5.286 – 7.254) [6]
xiii	1-ethyl-3-methylimidazolium methanesulfonate	$[C_2C_1Im][C_1SO_3]$	0.2732 (0.1889 – 0.3575) [b]	0.5355 (0.4502 – 0.6208) [b]
xiv	1-ethyl-3-methylimizolium acetate	$[C_2C_1Im][C_1CO_2]$	0.0740 (0 0700 – 0.0780) [b]	0.9133 (0.7108 – 1.115) [b]
xv	1-butyl-1-methylpyrrolidinium bromide	$[C_4C_1Pyr]Br$	2.733 [1]	*n.a.*
xvi	1-ethyl-1-methylpyrrolidinium methanesulfonate	$[C_2C_1Pyr][C_1SO_3]$	2.198 (2.031 – 2.365) [b]	1.798 (1.578 – 2.017) [b]
xvii	1-butyl-3-methylpyridinium bromide	$[C_4C_1Py]Br$	1.127 [1]	*n.a.*
xviii	1-butylpyridinium chloride	$[C_4Py]Cl$	*n.a.*	0.2575 (0.2232 – 0.2918) [9]

[a] Endpoint: yield.
[b] Data determined in this work.

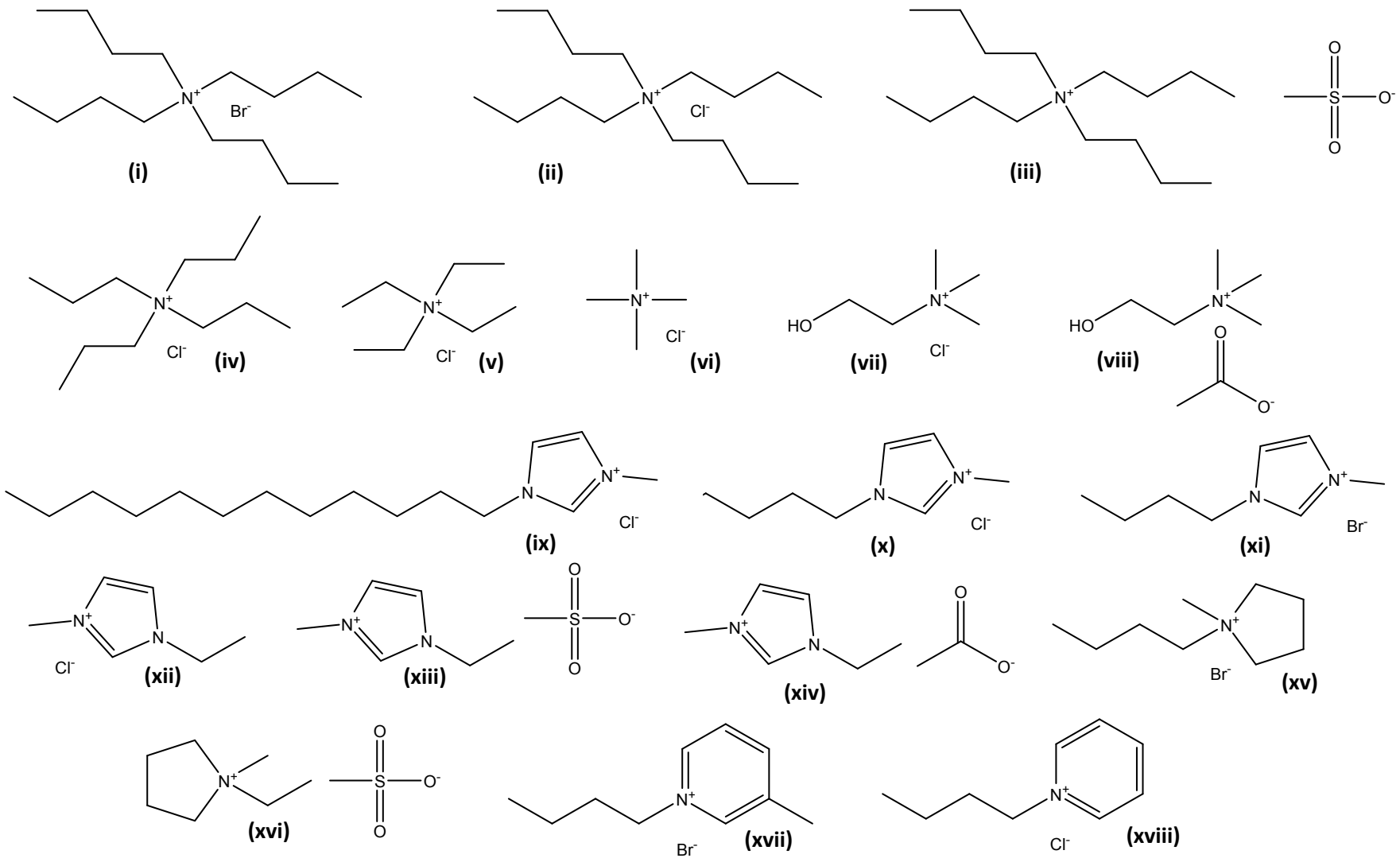

Figure S1. Ionic liquids chemical structures. Names and acronyms are presented in **Table S2**..

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