Supporting Information

Aqueous solutions of surface-active ionic liquids: remarkable alternative solvents to improve the solubility of triterpenic acids and their extraction from biomass

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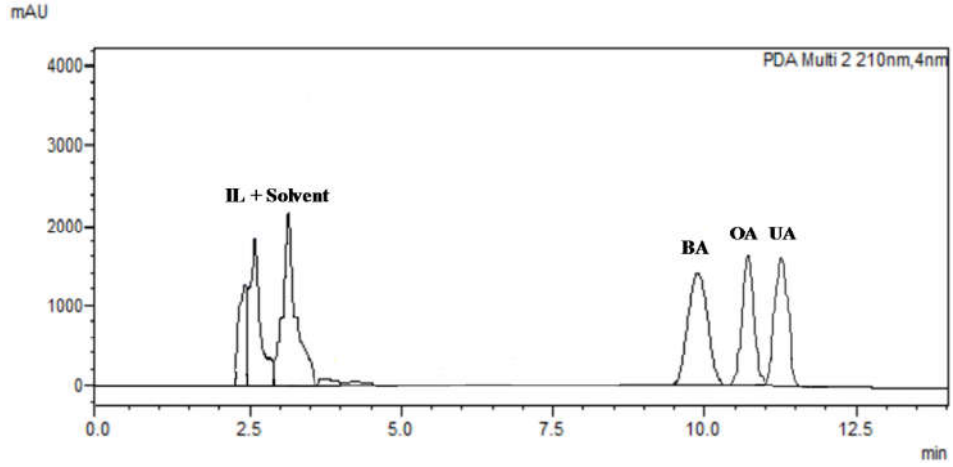
Figures/Tables

(a)



(b)

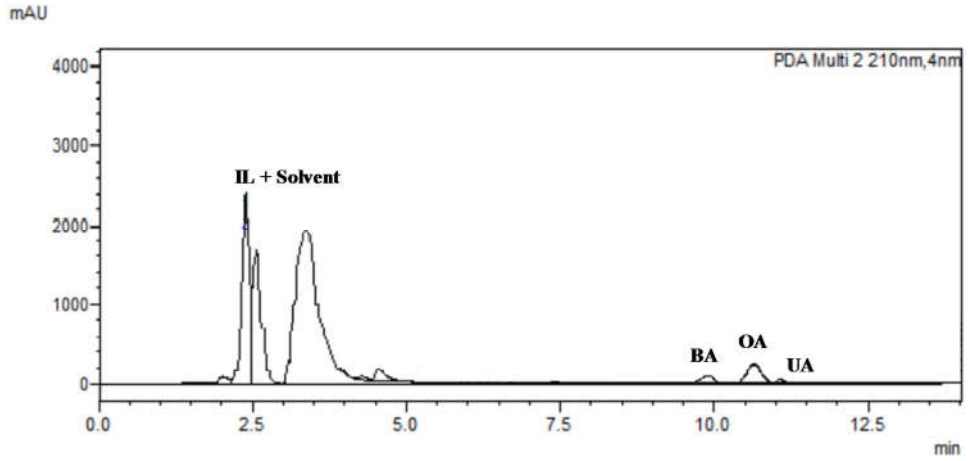


Fig. S1. Illustrative HPLC chromatograms corresponding to (a) standards TTAs, namely, UA, OA and BA, dissolved in an aqueous solutions of $[C_{14}C_1im]Cl$; (b) $[C_{14}C_1im]Cl$ (500 mM) aqueous solution after the extraction from apple peels at 80ºC (b).

Table S1. Solubility of ursolic acid in aqueous solutions of ILs at 30ºC.

Ionic Liquid/Concentration	[Ursolic Acid] ± σ / (g.L^{-1})					
	50 mM	**150 mM**	**250 mM**	**500 mM**	**750 mM**	**1000 mM**
[C_8C_1im]Cl	-	0.004 ± 0.001	0.028 ± 0.001	0.091 ± 0.003	0.280 ± 0.016	0.435 ± 0.007
[$C_{10}C_1$im]Cl	0.007 ± 0.000	0.192 ± 0.001	0.461 ± 0.009	1.008 ± 0.439	1.474 ± 0.048	1.612 ± 0.014
[$C_{12}C_1$im]Cl	0.059 ± 0.001	0.412 ± 0.009	0.699 ± 0.045	1.173 ± 0.068	1.544 ± 0.028	1.714 ± 0.052
[$C_{14}C_1$im]Cl	0.321 ± 0.007	0.544 ± 0.023	0.868 ± 0.008	1.656 ± 0.038	1.919 ± 0.005	2.852 ± 0.009
[$C_{16}C_1$im]Cl	0.227 ± 0.005	0.892 ± 0.010	1.404 ± 0.036	2.481 ± 0.057	0.815 ± 0.110	ND
[$C_{18}C_1$im]Cl	0.419 ± 0.019	1.180 ± 0.018	ND	ND	ND	ND
[C_4C_1im][$C_8H_{17}SO_4$]	0.179 ± 0.007	1.931 ± 0.001	3.130 ± 0.001	1.849 ± 0.005	1.549 ± 0.005	1.343 ± 0.050
[$P_{444,14}$]Cl	0.235 ± 0.003	0.299 ± 0.003	0.348 ± 0.003	0.370 ± 0.004	0.488 ±0.006	0.813 ± 0.029

*ND – Not determined.

Table S2. Solubility of ursolic acid in aqueous solutions of conventional surfactants at 30ºC.

Conventional Surfactant/Concentration	[Ursolic Acid] ± σ / (g.L^{-1})					
	50 mM	**150 mM**	**250 mM**	**500 mM**	**750 mM**	**1000 mM**
SDS	0.325 ± 0.001	1.350 ± 0.044	ND	ND	ND	ND
CTAB	0.078 ± 0.001	0.259 ± 0.002	0.980 ± 0.036	1.607 ± 0.009	ND	ND
SDBS	1.240 ± 0.077	2.092 ± 0.066	2.480 ± 0.045	ND	ND	ND

*ND – Not determined.

Table S3. CMC values of the studied surface-active ILs at 30ºC.

[Ionic Liquids]	CMC (mM) ± σ (measured)	Literature
[C_8C_1im]Cl	233.0 ± 1.4	238.0[1]
[$C_{10}C_1$im]Cl	58.7 ± 0.8	57.2[2]; 55.0[3]
[$C_{12}C_1$im]Cl	15.2 ± 0.9	15.1[3]; 13.5[4]
[$C_{14}C_1$im]Cl	3.9 ± 0.1	3.8[5]; 3.6[4]
[$C_{16}C_1$im]Cl	0.9 ± 0.2	0.9[3,4]/ 1.1[3]
[$C_{18}C_1$im]Cl	0.3 ± 0.03	0.4[2]; 0.4[3]
[C_4C_1im][$C_8H_{17}SO_4$]	30.3 ± 0.7	31.0[6]

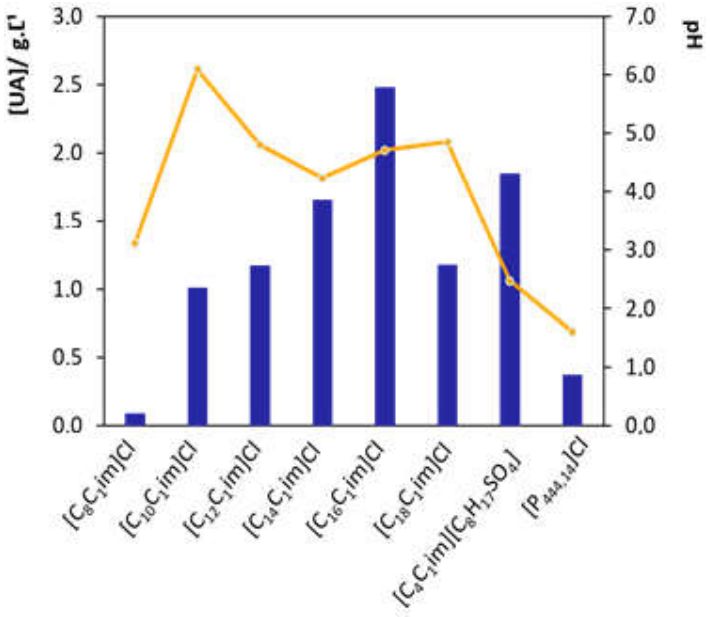


Fig. S2. pH ( ) and UA solubility ( ) in ILs aqueous solutions at 30°C.

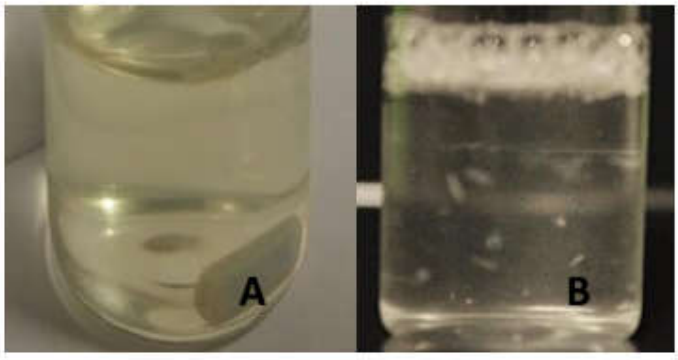


Fig. S3. Demonstration of the ability to use water as an anti-solvent in the precipitation of UA from an aqueous solution of [C_4C_1im][$C_8H_{17}SO_4$]. A: before water addition; B: after water addition.

Table S4. Extraction yields (EY) of TTAs (BA (betulinic), OA (oleanolic) and UA (ursolic) acids) from green apple peels with [$C_{14}C_1$im]Cl at different temperatures and fixed conditions ([IL] = 500mM, t = 60 min, $R_{S:L}$ = 1:10).

[$C_{14}C_1$im]Cl]	Triterpenic Acids	T / °C	EY ± σ / wt.%
500 mM	BA	25	ND
		50	0.071 ± 0.001
		80	0.898 ± 0.001
		90	0.105 ± 0.002
500 mM	OA	25	ND
		50	0.437 ± 0.002
		80	1.638 ± 0.001
		90	1.561 ± 0.001
500 mM	UA	25	ND
		50	0.042 ± 0.001
		80	0.081 ± 0.002
		90	0.072 ± 0.002

*ND – Not determined.

Table S5. Extraction yields of TTAs (BA, OA and UA) extracted from green apple peels with volatile organic solvents at fixed conditions (T = 80°C under reflux, t = 60 min, $R_{S:L}$ = 1:10).

Solvent	Triterpenic Acids	EY ± σ / wt.%
Acetone	BA	0.824 ± 0.003
	OA	0.450 ± 0.006
	UA	0.090 ± 0.002
Chloroform	BA	1.393 ± 0.005
	OA	1.049 ± 0.001
	UA	0.032 ± 0.002

References

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