Supplementary Material (ESI) for Green Chemistry

Supporting Information

High-performance extraction of alkaloids using aqueous two-phase systems with ionic liquids

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Experimental Procedure

Nicotine, > 99 wt % pure, was purchased from Sigma-Aldrich while caffeine, > 98.5 wt % pure, was acquired at Marsing & Co. Ltd. A/S. All ionic liquids (ILs) were commercially acquired at Iolitec, with the exception of $[C_4mim][CF_3CO_2]$ that was purchased from Solchemar. ILs individual samples were dried under constant conditions at moderate vacuum and temperature, for a minimum of 48 h, before use. The purity of each IL was further checked by ^1H, ^{13}C, and ^{19}F NMR spectra and found to be superior to 99 wt % for all samples. Urea, 99 wt % pure, was supplied by Panreac and used without further purification. K_3PO_4, 98 wt % pure, and NaCl, 99.9 % wt % pure, were from Sigma and Normapur, respectively. In order to remove water, the inorganic salts were dried under vacuum for a minimum of 12 h before use. Water used was ultrapure water, double distilled, passed by a reverse osmosis system and finally treated with a Milli-Q plus 185 water purification equipment.

Synthetic human urine aqueous phases were prepared by dissolution of urea and NaCl, in pure water, at the concentrations of 1.2 $g \cdot dm^{-3}$ and 4.0 $g \cdot dm^{-3}$, respectively. The alkaloids quantification, in both phases, was carried out by UV spectroscopy using a SHIMADZU UV-1700, Pharma-Spec spectrometer, at a wavelength of 274 nm or 261 nm for caffeine and nicotine, respectively, and using calibration curves previously established. Initial concentrations of caffeine and nicotine for phase distribution at the water ternary composition were, respectively, 2.6×10^{-2} $mol \cdot dm^{-3}$ and 2.5×10^{-2} $mol \cdot dm^{-3}$. Possible interferences of both the inorganic salt and the IL with the analytical method were taken into account and blank controls were employed whenever necessary. The partition coefficients of caffeine (K_{caf}) or nicotine (K_{nic}) are defined as the ratio between the concentration of the alkaloids in the IL- and K_3PO_4-rich phases.

Partition Coefficients and Extraction Efficiencies

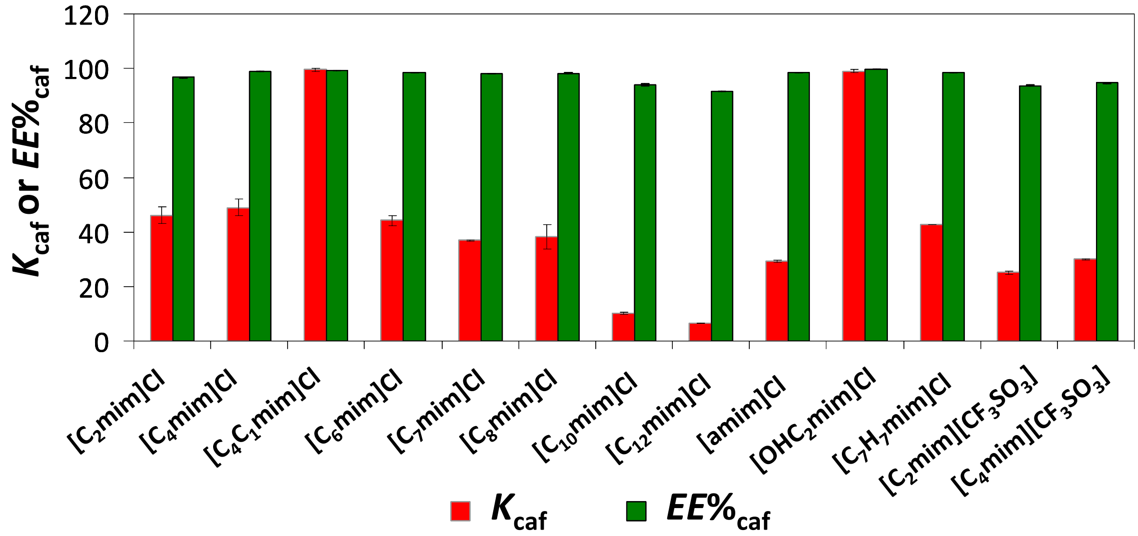

Fig. S1. Partition coefficients (K_{caf}) and extraction efficiencies percentages ($EE\%_{caf}$) of caffeine in chloride-based ILs/K_3PO_4 ABS at 298 K (IL at 25 wt % and K_3PO_4 at 15 wt %, except for [C_7H_7mim]Cl at 40 wt % and K_3PO_4 at 15 wt %).

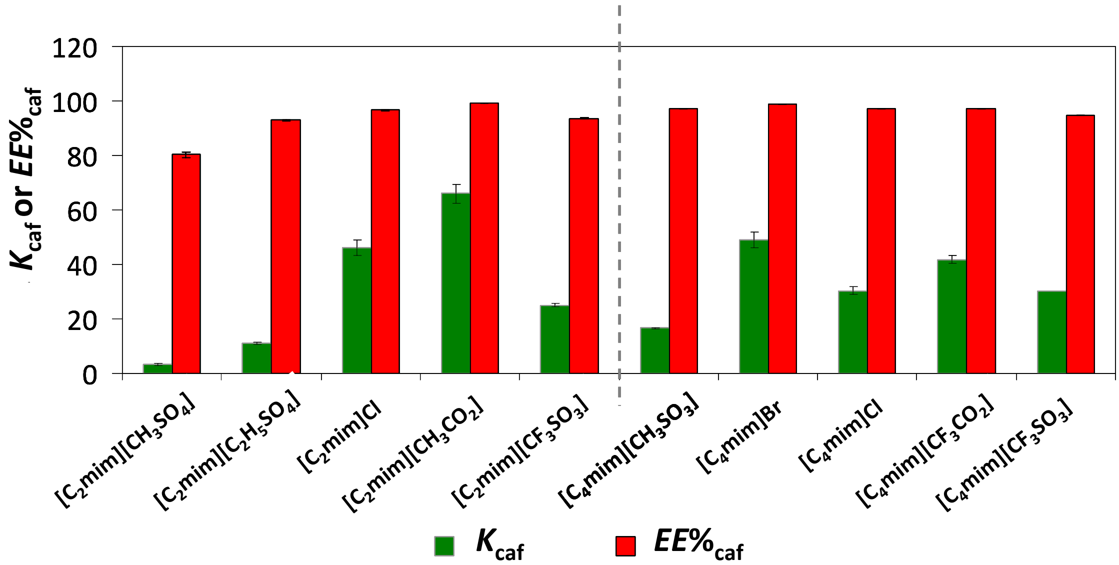

Fig. S2. Partition coefficients (K_{caf}) and extraction efficiencies percentages ($EE\%_{caf}$) of caffeine in [C_2mim]- and [C_4mim]-based ILs/K_3PO_4 ABS at 298 K (IL at 25 wt % and K_3PO_4).

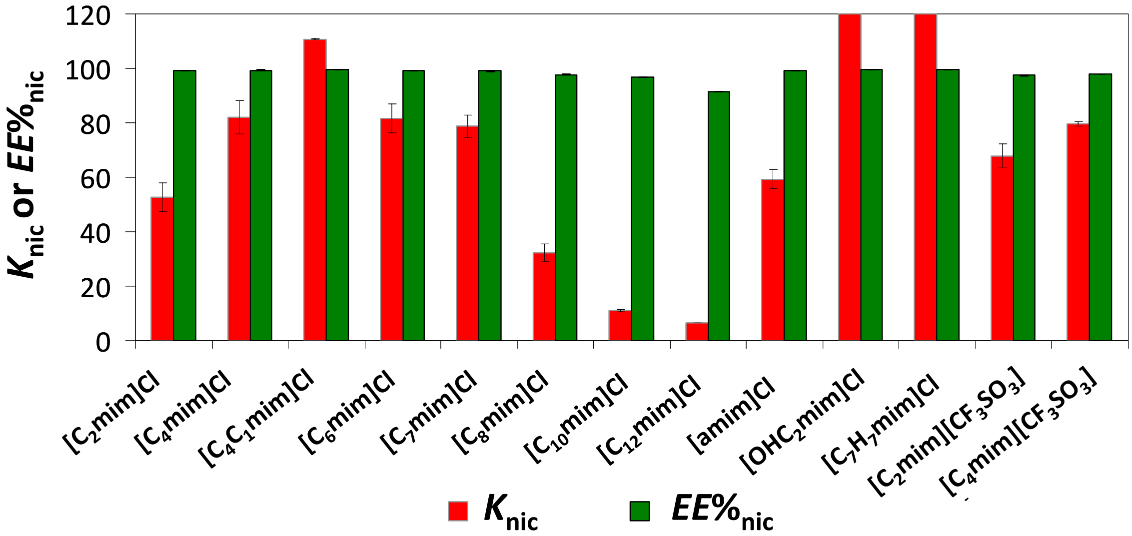

Fig. S3. Partition coefficients (K_{nic}) and extraction efficiencies percentages ($EE\%_{nic}$) of nicotine in chloride-based ILs/K_3PO_4 ABS at 298 K (IL at 25 wt % and K_3PO_4 at 15 wt %, except for [C_7H_7mim]Cl at 40 wt % and K_3PO_4 at 15 wt %).

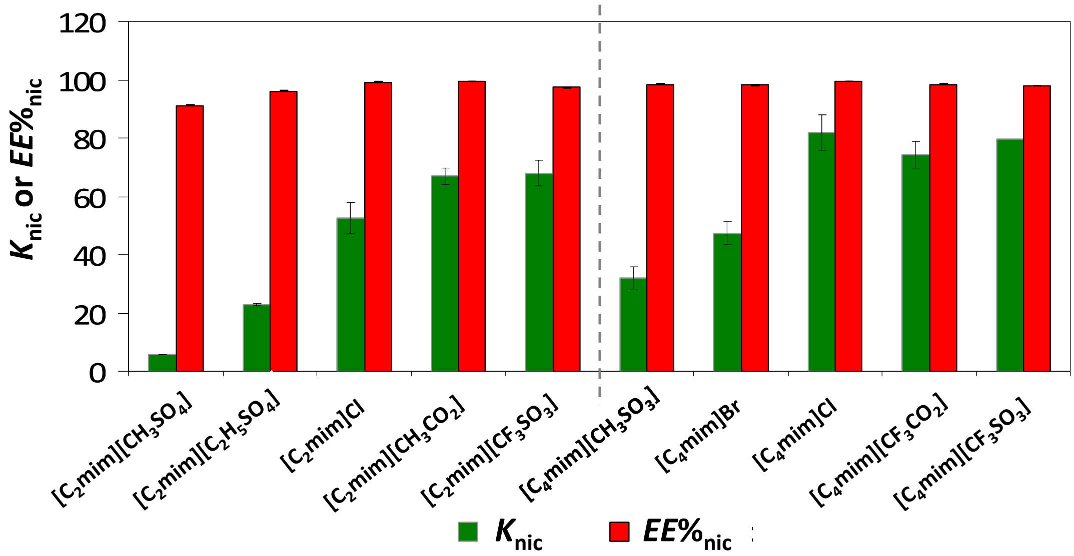

Fig. S4. Partition coefficients (K_{nic}) and extraction efficiencies percentages ($EE\%_{nic}$) of nicotine in [C_2mim]- and [C_4mim]-based ILs/K_3PO_4 ABS at 298 K (IL at 25 wt % and K_3PO_4).

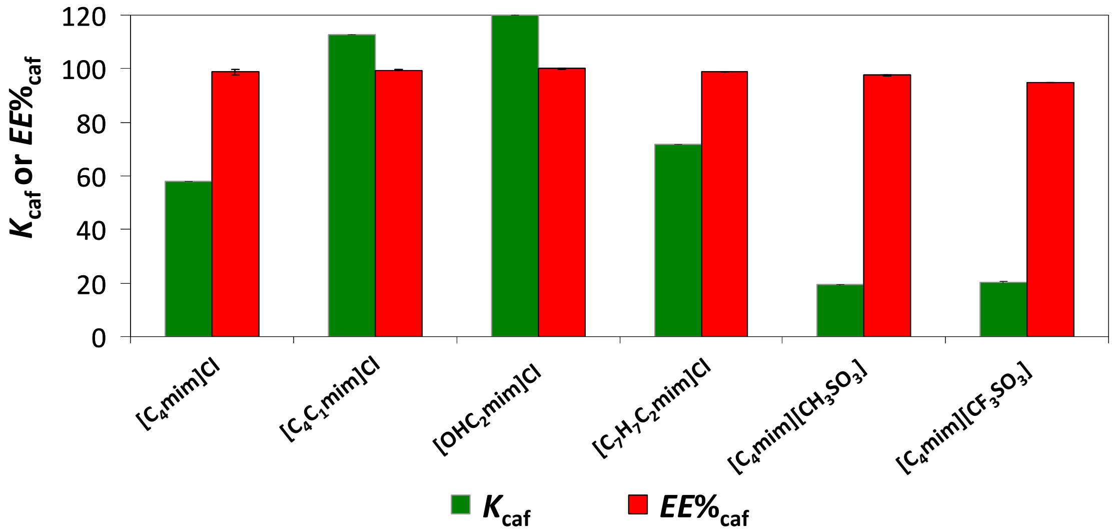

Fig. S5. Partition coefficients (K_{caf}) and extraction efficiencies percentages ($EE\%_{caf}$) of caffeine in human urine-based ILs/K_3PO_4 ABS at 298 K (IL at 25 wt % and K_3PO_4 at 15 wt %, except for [C_7H_7mim]Cl at 40 wt % and K_3PO_4 at 15 wt %).

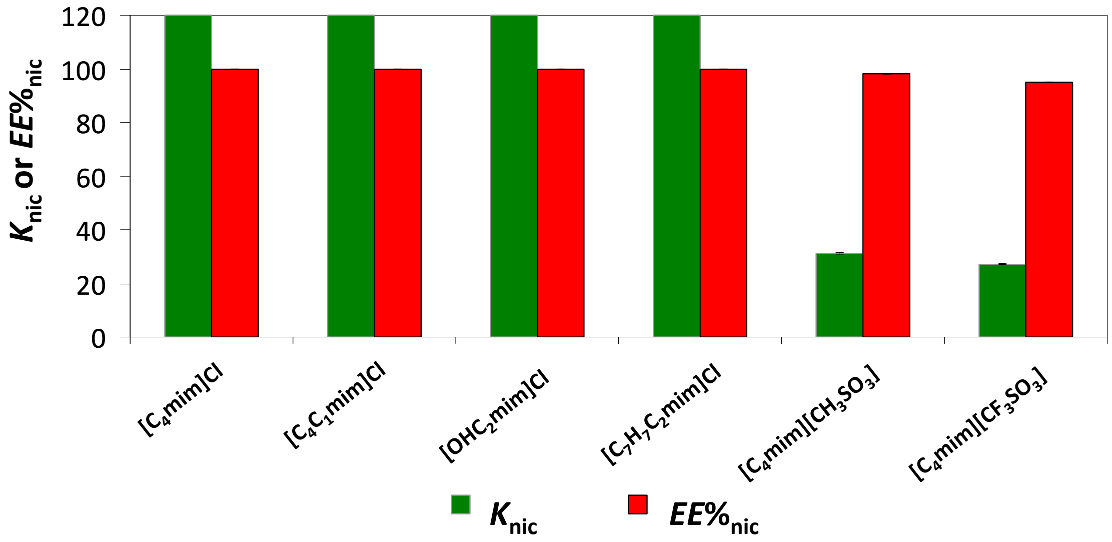

Fig. S6. Partition coefficients (K_{nic}) and extraction efficiencies percentages ($EE\%_{nic}$) of nicotine in human urine-based ILs/K_3PO_4 ABS at 298 K (IL at 25 wt % and K_3PO_4 at 15 wt %, except for [C_7H_7mim]Cl at 40 wt % and K_3PO_4 at 15 wt %).

Table S1. Weight fraction composition, partition coefficients and extraction efficiencies of caffeine in IL-based ABS and respective tie-lines (TLs) and tie-line lengths (TLLs)

IL	wt %		TL equation IL (wt %) = $a + b \cdot K_3PO_4$ (wt %)		TLL	$K_{caf} \pm \sigma^a$	$EE\%_{caf} \pm \sigma^a$
	IL	K_3PO_4	a	b			
$[C_2mim]Cl$	25.185	14.962	42.205	-1.138	43.386	46.1 ± 2.9	96.70 ± 0.20
$[C_2mim]Cl$	40.093	15.129	58.722	-1.231	73.811	120	100
$[C_4mim]Cl$	24.361	14.923	42.269	-1.200	44.493	49.0 ± 2.9	98.89 ± 0.07
$[C_4mim]Cl$	30.320	14.760	49.407	-1.293	57.788	120	100
$[C_4mim]Cl$	34.989	15.479	55.708	-1.339	67.523	120	100
$[C_4mim]Cl$	39.855	15.004	59.968	-1.341	73.856	120	100
$[C_4mim]Cl$	44.853	15.040	66.399	-1.433	80.650	120	100
$[C_4C_1mim]Cl$	25.127	15.080	44.154	-1.262	47.966	99.6 ± 0.6	99.41 ± 0.03
$[C_6mim]Cl$	24.921	14.856	46.455	-1.450	45.907	44.1 ± 1.8	98.53 ± 0.06
$[C_7mim]Cl$	25.066	15.166	49.496	-1.611	44.417	37.0 ± 0.2	97.96 ± 0.01
$[C_8mim]Cl$	25.068	15.073	50.675	-1.699	36.784	38.2 ± 4.6	98.16 ± 0.22
$[C_{10}mim]Cl$	25.046	15.207	53.181	-1.850	24.853	10.1 ± 0.5	94.01 ± 0.26
$[C_{12}mim]Cl$	25.038	15.014	51.344	-1.752	27.518	6.65 ± 0.01	91.61 ± 0.01
[amim]Cl	24.262	15.293	42.449	-1.189	42.842	29.4 ± 0.3	98.32 ± 0.02
[amim]Cl	30.023	14.813	47.901	-1.207	56.670	120	100
[amim]Cl	35.148	14.956	54.115	-1.268	66.449	120	100
[amim]Cl	40.132	14.871	60.586	-1.375	73.839	120	100
[amim]Cl	44.817	15.193	64.543	-1.298	81.148	32.3 ± 0.3	98.47 ± 0.04
$[OHC_2mim]Cl$	39.963	15.049	85.826	-3.048	63.673	98.9 ± 0.6	99.69 ± 0.02
$[C_7H_7mim]Cl$	25.123	14.925	50.512	-1.701	43.036	42.62 ± 0.06	98.26 ± 0.02
$[C_7H_7mim]Cl$	30.105	14.962	55.816	-1.718	56.054	120	100
$[C_7H_7mim]Cl$	34.893	15.001	60.784	-1.726	65.219	120	100
$[C_7H_7mim]Cl$	40.057	14.930	66.055	-1.741	73.246	120	100
$[C_7H_7mim]Cl$	44.996	14.930	69.071	-1.613	79.476	120	100
$[C_7H_7mim]Cl$	49.962	14.883	75.540	-1.719	86.458	90.0 ± 5.7	99.51 ± 0.04
$[C_7H_7mim]Cl$	25.152	19.997	59.596	-1.723	63.229	120	100
$[C_7H_7mim]Cl$	25.053	25.067	66.647	-1.659	75.361	120	100
$[C_7H_7mim]Cl$	25.130	29.832	71.663	-1.560	83.829	120	100
$[C_2mim][CF_3SO_3]$	24.996	14.891	69.540	-2.991	61.973	25.1 ± 0.8	93.59 ± 0.18
$[C_4mim][CF_3SO_3]$	24.996	15.352	70.967	-2.995	70.428	30.0 ± 0.2	94.70 ± 0.04
$[C_2mim][CH_3SO_4]$	25.007	15.178	51.644	-1.755	31.551	3.3 ± 0.5	80.27 ± 1.05
$[C_2mim][C_2H_5SO_4]$	24.853	15.648	54.162	-1.873	44.687	11.1 ± 0.3	92.86 ± 0.18
$[C_2mim][CH_3CO_2]$	25.172	14.931	39.995	-0.993	48.132	66.0 ± 3.6	99.34 ± 0.04
$[C_4mim]Br$	24.822	15.085	50.345	-1.692	45.396	30.4 ± 1.3	97.18 ± 0.11
$[C_4mim][CH_3SO_3]$	24.917	15.090	44.622	-1.306	38.919	16.6 ± 0.2	96.98 ± 0.04
$[C_4mim][CF_3CO_2]$	24.785	15.475	58.626	-2.187	56.984	41.8 ± 1.6	97.09 ± 0.14

[a]associated standard deviation

Table S2. Weight fraction composition, partition coefficients and extraction efficiencies of nicotine in IL-based ABS and respective tie-lines (TLs) and tie-line lengths (TLLs)

IL	wt %		TL equation IL (wt %) = $a + b{\cdot}K_3PO_4$ (wt %)		TLL	$K_{nic} \pm \sigma^a$	$EE\%_{nic} \pm \sigma^a$
	IL	K_3PO_4	a	b			
$[C_2mim]Cl$	25.292	14.778	41.527	-1.099	43.583	52.7 ± 5.3	99.18 ± 0.08
$[C_2mim]Cl$	40.093	15.129	51.916	-1.237	73.950	58.7 ± 2.7	99.31 ± 0.03
$[C_4mim]Cl$	25.569	14.882	43.662	-1.216	47.673	82.1 ± 6.1	99.34 ± 0.05
$[C_4mim]Cl$	29.990	16.281	51.758	-1.337	60.914	120	100
$[C_4mim]Cl$	35.005	15.271	56.611	-1.415	67.114	120	100
$[C_4mim]Cl$	39.832	14.876	60.539	-1.392	73.521	120	100
$[C_4mim]Cl$	45.014	15.279	66.739	-1.422	81.312	120	100
$[C_4mim]Cl$	49.957	15.159	71.248	-1.405	87.410	95.5 ± 1.3	99.51 ± 0.03
$[C_4C_1mim]Cl$	25.007	15.170	44.057	-1.256	47.953	110.7 ± 0.2	99.47 ± 0.01
$[C_6mim]Cl$	25.125	14.891	47.112	-1.477	46.634	81.7 ± 5.4	99.17 ± 0.05
$[C_7mim]Cl$	25.014	15.263	49.737	-1.620	44.798	78.8 ± 4.0	99.01 ± 0.05
$[C_8mim]Cl$	25.010	15.079	50.901	-1.717	36.597	32.1 ± 3.3	97.71 ± 0.23
$[C_{10}mim]Cl$	24.992	15.146	53.162	-1.860	23.302	11.0 ± 0.3	96.72 ± 0.09
$[C_{12}mim]Cl$	25.000	15.010	51.576	-1.771	27.095	6.5 ± 0.1	91.49 ± 0.10
[amim]Cl	24.945	15.198	43.838	-1.773	44.833	59.3 ± 3.6	99.17 ± 0.05
[amim]Cl	29.895	14.931	47.853	-1.203	56.717	120	100
[amim]Cl	34.916	15.013	53.812	-1.259	66.201	120	100
[amim]Cl	39.761	15.222	53.383	-1.223	74.348	120	100
[amim]Cl	45.146	15.093	63.720	-1.231	81.772	120	100
$[OHC_2mim]Cl$	40.072	14.915	86.128	-3.088	63.369	120	100
$[C_7H_7mim]Cl$	25.081	14.807	50.444	-1.691	43.240	120	100
$[C_7H_7mim]Cl$	30.100	15.043	47.689	-1.169	54.397	120	100
$[C_7H_7mim]Cl$	35.183	15.013	60.969	-1.718	65.685	120	100
$[C_7H_7mim]Cl$	40.873	15.017	65.921	-1.668	74.182	120	100
$[C_7H_7mim]Cl$	45.070	14.987	69.977	-1.662	79.952	120	100
$[C_7H_7mim]Cl$	49.923	15.001	73.733	-1.554	86.007	120	100
$[C_7H_7mim]Cl$	25.081	14.807	50.444	-1.691	43.241	120	100
$[C_7H_7mim]Cl$	24.991	20.053	59.757	-1.734	63.292	120	100
$[C_7H_7mim]Cl$	25.047	25.021	66.908	-1.673	75.522	120	100
$[C_7H_7mim]Cl$	25.222	30.159	74.701	-1.641	86.515	120	100
$[C_2mim][CF_3SO_3]$	24.983	15.124	70.755	-3.027	63.646	67.9 ± 4.4	97.46 ± 0.16
$[C_4mim][CF_3SO_3]$	25.080	14.957	67.901	-2.863	65.409	79.6 ± 0.9	97.89 ± 0.02
$[C_2mim][CH_3SO_4]$	24.846	14.670	49.547	-1.684	24.412	5.7 ± 0.2	91.17 ± 0.22
$[C_2mim][C_2H_5SO_4]$	24.185	16.381	52.733	-1.743	45.780	22.8 ± 0.5	96.12 ± 0.08
$[C_2mim][CH_3CO_2]$	24.933	15.571	39.046	-0.936	48.787	66.9 ± 2.9	99.28 ± 0.03
$[C_4mim]Br$	25.046	14.937	50.237	-1.686	45.300	47.3 ± 4.0	98.24 ± 0.15
$[C_4mim][CH_3SO_3]$	24.998	14.979	44.769	-1.320	38.511	32.1 ± 3.8	98.38 ± 0.19
$[C_4mim][CF_3CO_2]$	24.933	14.779	56.326	-2.124	53.478	74.2 ± 4.7	98.47 ± 0.10

[a]associated standard deviation

Table S3. Weight fraction composition, partition coefficients and extraction efficiencies, of caffeine and nicotine, in human urine-based ILs/K_3PO_4 ABS at 298 K

IL	wt %		$K_{caf} \pm \sigma^a$	$EE\%_{\mathrm{caf}} \pm \sigma^a$	wt %		$K_{\mathrm{nic}} \pm \sigma^a$	$EE\%_{\mathrm{nic}} \pm \sigma^a$
	IL	K_3PO_4			IL	K_3PO_4		
[C_4mim]Cl	25.117	14.997	57.8 ± 0.1	98.80 ± 0.01	24.844	14.937	120	100
[C_4C_1mim]Cl	24.896	15.119	112.7 ± 0.5	99.45 ± 0.07	24.889	15.275	120	100
[OHC_2mim]Cl	40.224	14.891	120	100	40.235	15.046	120	100
[C_7H_7mim]Cl	24.952	15.096	71.8 ± 0.2	98.88 ± 0.01	24.891	15.057	120	100
[C_4mim][CH_3SO_3]	25.050	14.982	19.3 ± 0.5	97.51 ± 0.07	24.837	15.513	31.1 ± 0.3	98.27 ± 0.02
[C_4mim][CF_3SO_3]	24.959	15.078	20.2 ± 1.7	94.97 ± 0.41	24.902	15.281	27.2 ± 0.2	94.95 ± 0.03

[a]associated standard deviation