

Supporting Information

Simultaneous extraction and concentration of water pollution tracers using ionic-liquid-based systems

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Experimental procedure

Determination of phase diagrams and tie-lines

An aqueous solution of $K_3C_6H_5O_7$ at *ca.* 50 wt% and an aqueous solution of $[C_4C_1C_1im]Cl$ at approximately 85 wt% were gravimetrically prepared and used to determine the respective binodal curve/ternary phase diagram. Repetitive drop-wise addition of the organic salt solution to the IL aqueous solution was carried out until the detection of a cloudy mixture. Then, repetitive drop-wise of double distilled water was added until the detection of a clear and limpid mixture. It should be noted that the addition of the IL aqueous solution to the salt solution was also carried out to complete the phase diagram. The ternary system compositions were determined by weight quantification of all components added to the mixture within $\pm 10^{-4}$ g. The experimental solubility data were fitted according to Eq. SI-1:

$$[IL] = A \exp[(B \times [salt]^{0.5}) - (C \times [salt]^3)] \quad (SI-1)$$

The tie-lines (TLs) were determined by a gravimetric method originally described by Merchuk *et al.* [1], well established in the literature [2-6]. Several ternary systems were prepared within the biphasic region at a constant weight fraction percentage: 40 wt % of IL + 20 wt % of $K_3C_6H_5O_7$ + 40 wt % of H_2O . The ternary mixtures were left to equilibrate for at least 12 h at (298 ± 1) K. Then, the top and bottom phases were separated and weighted. For the determination of the TLs, it was used the following system of four equations (Eq. SI-2 to SI-5) with four unknown variables ($[IL]_{IL}, [salt]_{IL}, [IL]_{salt}, [salt]_{salt}$):

$$[IL]_{IL} = A \exp(B[salt]_{IL}^{0.5} - C[salt]_{IL}^3) \quad (SI-2)$$

$$[IL]_{salt} = A \exp(B[salt]_{salt}^{0.5} - C[salt]_{salt}^3) \quad (SI-3)$$

$$[IL]_{IL} = \frac{[IL]_M}{\alpha} - \left(\frac{1-\alpha}{\alpha}\right) [IL]_{salt} \quad (SI-4)$$

$$[salt]_{IL} = \frac{[salt]_M}{\alpha} - \left(\frac{1-\alpha}{\alpha}\right)[salt]_{salt} \quad (SI-5)$$

where the indexes M , IL and $salt$ correspond to the mixture, IL-rich phase and salt-rich phase, respectively. The parameter α is the ratio between the IL-rich phase and the total mixture weight. In this way, the concentration of IL and organic salt on the top and bottom phases can be determined in a given mixture point at the biphasic region.

The tie-line lengths (TLL) were calculated through Eq. SI-6:

$$TLL = \sqrt{([salt]_{IL} - [salt]_{salt})^2 + ([IL]_{IL} - [IL]_{salt})^2} \quad (SI-6)$$

Tie-line analytical quantification

After the equilibration of the mixture constituted by 33 wt % of IL + 25 wt % of $K_3C_6H_5O_7$ + 42 wt % H_2O , for a phase volume ratio equal to 1, the coexisting phases were separated and analytically quantified. The $[N_{4444}]Cl$ concentration in each phase was determined by chloride quantification using a Metrohm 904 Titrando ion chloride electrode, using a previously established calibration curve. The calibration curve was determined with standard solutions with appropriate concentrations of chloride ions (between $0.1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ and $100 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$). All the measurements were performed at fixed ionic strength through the addition of a Total Ionic Strength Adjustment Buffer (TISAB) solution to all the standards and samples. The TISAB solution was prepared by mixing aqueous solutions at $0.1 \text{ mol} \cdot \text{L}^{-1}$ of KNO_3 , CH_3COOH , and $NaC_2H_3O_2$. The water content in each phase was determined by evaporation, for which each phase was dried in an air oven at $\sim 373 \text{ K}$, until a constant weight of the non-volatile mixture $[N_{4444}]Cl + K_3C_6H_5O_7$ (within $\pm 10^{-4} \text{ g}$) was obtained. The amount of $K_3C_6H_5O_7$ was determined by weight difference. This process was carried out in triplicate to ascertain on the average values and associated standard deviations. The respective TL and composition of the coexisting phases analytically determined was found to be in good agreement to that established in the literature obtained by a gravimetric method [5].

Results

Table SI-1. Weight fraction compositions (wt %) for the TLs corresponding to the ternary systems composed of IL + $K_3C_6H_5O_7$ + H_2O at 298 K. Legend: IL-rich phase (IL), initial mixture (M) and salt-rich phase (salt).

IL	Weight fraction composition (wt %)								TLL
	[IL] _{IL}	[Salt] _{IL}	pH _{IL}	[IL] _M	[Salt] _M	[IL] _{Salt}	[Salt] _{Salt}	pH _{Salt}	
[C ₄ C ₁ im][CF ₃ SO ₃]	84.50	1.19	8.10	40.54	18.96	1.02	34.93	8.31	90.04
[C ₄ C ₁ im][N(CN) ₂]	85.81	0.62	6.70	39.81	20.12	0.31	36.87	9.00	92.87
[C ₄ C ₁ im][SCN]	72.91	1.16	8.24	39.57	19.94	0.00	42.23	8.00	83.68
[C ₄ C ₁ im]Br	62.53	2.93	8.49	39.22	20.15	2.18	48.65	8.40	74.73
[C ₄ C ₁ im]Cl	51.10	8.22	8.41	39.34	20.05	6.69	52.86	8.15	62.97
[N ₄₄₄₄]Cl [5]	64.74	1.81	9.58	39.87	20.21	1.36	48.71	9.32	78.84
[P ₄₄₄₄]Cl	66.65	3.74	8.13	39.54	20.02	2.06	42.53	7.54	75.34
[C ₄ C ₁ pyr]Cl	54.77	4.83	9.60	40.01	19.97	4.71	56.18	7.08	71.71
[C ₄ C ₁ pip]Cl	52.77	5.69	9.39	39.73	20.06	2.39	61.23	8.16	74.99
[C ₄ C ₁ C ₁ im]Cl	52.57	7.91	9.12	40.76	19.59	3.66	60.78	9.12	72.02

Table SI-2. HPLC-UV optimized conditions to quantify CAF and CBZ. Legend: Solvent A: water; Solvent B: acetonitrile.

Time (min)	Solvent A (vol %)	Solvent B (vol %)	Wavelength (nm)
<i>CAF</i>			
0	75	25	272
2	57.5	42.5	272
4	40	60	272
6	40	60	272
8	40	60	272
10		<i>End</i>	
<i>CBZ</i>			
0	75	25	285
2	57.5	42.5	285
4	60	40	285
6	60	40	285
8	60	40	285
20		<i>End</i>	
<i>Mixture of CAF and CBZ in model aqueous solutions</i>			
0	75	25	272
2	57.5	42.5	272
4	55	45	285
6	55	45	285
8	55	45	285
10		<i>End</i>	
<i>Mixture of CAF and CBZ in the wastewater effluent sample</i>			
0	75	25	272
2	57.5	42.5	272
4	57.5	42.5	285
6	57.5	42.5	285
8	57.5	42.5	285
10		<i>End</i>	

Table SI-3. Experimental weight fraction data of the binodal curve of the system composed of [C₄C₁C_{1im}]Cl (1) + K₃C₆H₅O₇ (2) + H₂O (3) at (298 ± 1) K and atmospheric pressure.

100 w₁	100 w₂	100 w₁	100 w₂
63.414	3.326	39.822	17.276
59.024	4.639	38.904	17.956
56.281	5.895	38.331	18.562
53.565	7.177	37.583	19.172
49.974	9.314	36.763	19.858
49.042	10.326	35.916	20.634
48.052	10.918	35.066	21.453
47.685	11.182	34.195	22.281
47.002	11.550	33.520	23.003
46.370	11.901	31.892	24.260
45.932	12.208	31.168	25.133
45.172	12.659	29.796	26.404
44.501	13.086	28.927	27.405
44.279	13.526	27.395	28.849
44.182	13.799	25.668	30.580
43.645	14.196	24.418	32.060
43.002	14.677	23.131	33.561
42.637	15.069	20.774	35.743
41.942	15.586	19.068	37.643
41.170	16.130	17.285	39.752
40.370	16.757		

Table SI-4. Fitting parameters used to describe the experimental liquid-liquid phase diagram data by Eq. SI-1 for the system composed of [C₄C₁C₁im]Cl + K₃C₆H₅O₇ + H₂O.

$A \pm \sigma$	87.7 ± 0.4
$B \pm \sigma$	-0.181 ± 0.004
$10^5(C \pm \sigma)$	0.787 ± 0.014
R^2	0.9997

Table S5. Percentage extraction efficiencies of CAF and CBZ ($EE_{CAF}\%$ and $EE_{CBZ}\%$, respectively) with the systems composed of IL + K₃C₆H₅O₇ + H₂O and respective initial mixture compositions.

IL	Weight fraction		$EE_{CAF}\% \pm \sigma$	$EE_{CBZ}\% \pm \sigma$
	composition / (wt %)			
	[IL] _M	[Salt] _M		
[C ₄ C ₁ im][CF ₃ SO ₃]	39.97	19.94	96.57 ± 0.03	99.92 ± 0.02
[C ₄ C ₁ im][N(CN) ₂]	39.86	20.07	99.18 ± 0.13	100.00 ± 0.20
[C ₄ C ₁ im][SCN]	39.87	20.06	98.68 ± 0.04	99.97 ± 0.01
[C ₄ C ₁ im]Br	40.02	19.95	97.56 ± 0.36	99.83 ± 0.05
[C ₄ C ₁ im]Cl	40.46	19.81	98.52 ± 0.04	99.64 ± 0.06
[N ₄₄₄₄]Cl	39.70	20.04	99.61 ± 0.16	100.00 ± 0.20
[P ₄₄₄₄]Cl	39.52	20.10	99.59 ± 0.09	100.00 ± 0.20
[C ₄ C ₁ pyr]Cl	40.06	19.98	98.88 ± 0.05	99.80 ± 0.01
[C ₄ C ₁ pip]Cl	39.63	20.14	95.21 ± 0.20	99.88 ± 0.01
[C ₄ C ₁ C ₁ im]Cl	40.74	19.78	98.57 ± 0.36	99.25 ± 0.09

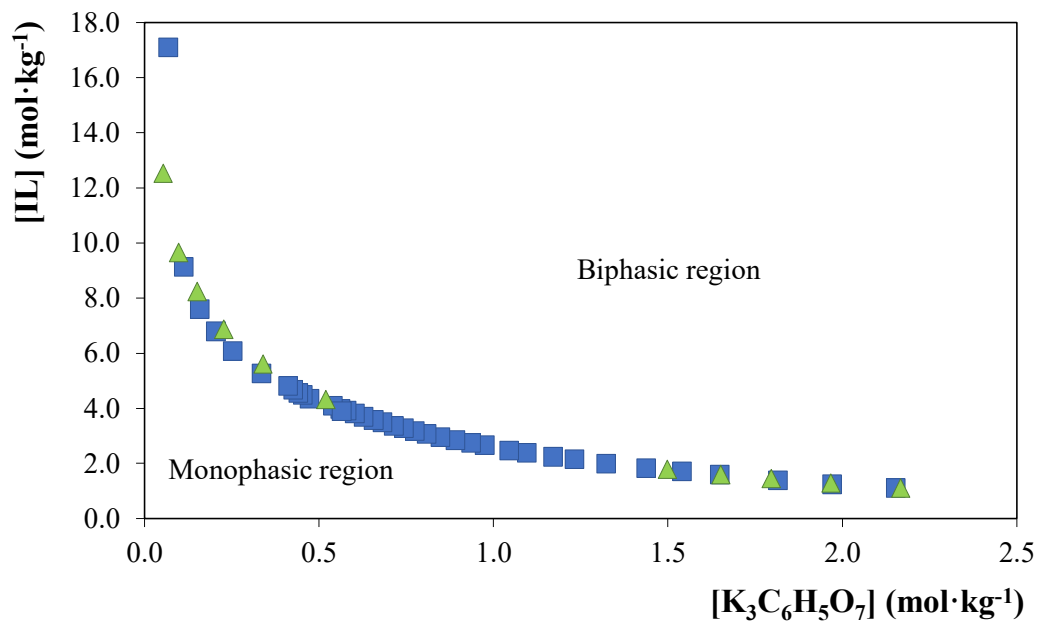


Figure SI-1. Ternary phase diagrams of aqueous biphasic systems composed of IL + $\text{K}_3\text{C}_6\text{H}_5\text{O}_7$ + H_2O , at (298 ± 1) K and at atmospheric pressure: $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ (\blacktriangle) [5], and $[\text{C}_4\text{C}_1\text{C}_1\text{im}]\text{Cl}$ (\blacksquare).

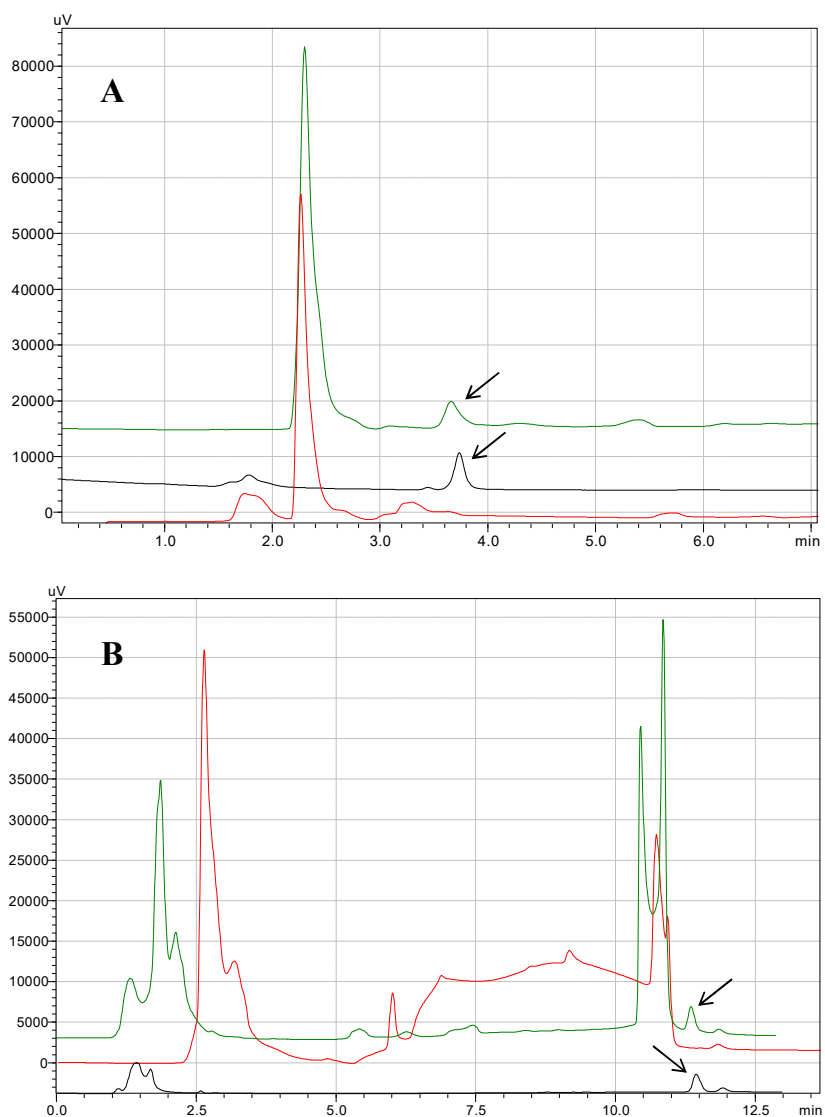


Figure SI-2. HPLC-UV chromatograms corresponding to the identification/quantification of pollution tracers individually extracted at laboratory standard conditions. **(A)** Chromatograms for the identification and quantification of CAF; **(B)** Chromatograms for the identification and quantification of CBZ. Chromatograms of standard solutions of CAF and CBZ (black line), chromatograms of aqueous solutions of CAF and CBZ extracted into the $[N_{4444}]Cl$ -rich phase (green line) and chromatograms of the $[N_{4444}]Cl$ -rich as control without added pollution tracers (red line).

Table S6. Chromatographic data for the quantification of CAF and CBZ, including the retention time ($t_{\text{retention}}$), peak area (A_{peak}), percentage recoveries with the respective standard deviation values, and concentration factor (CF) values obtained in this work. The percentage recovery (% R) of CAF and CBZ was given by ratio between peak area values of the pollution tracer concentrated in the IL-rich phase and those for the individual standard stock aqueous solutions. The final concentration achieved for both CAF and CBZ in the IL-rich phase is $1 \times 10^{-3} \text{ g}\cdot\text{dm}^{-3}$.

System	Tracer	$t_{\text{retention}} / \text{min}$	% R $\pm \sigma$	CF
Single extraction	CAF	3.7	98	48.8
Single extraction	CBZ	11.3	125	47.8
Simultaneous extraction	CAF	3.7	91 \pm 15	45.8
	CBZ	7.1	106 \pm 0.1	45.8
Wastewater effluent sample	CAF	3.9	90 \pm 16	45.9
	CBZ	9.7	87 \pm 9	45.9
Blank control	(---)	(---)	(---)	51.3

Table S7. Solubility data of the two pollution tracers (CBZ and CAF) in water [7] and in the IL-rich phase of the system composed of $[\text{N}_{4444}]\text{Cl} + \text{K}_3\text{C}_6\text{H}_5\text{O}_7 + \text{H}_2\text{O}$ at $(298 \pm 1) \text{ K}$ and atmospheric pressure.

Pharmaceutical	Solubility in water / ($\text{g}\cdot\text{L}^{-1}$)	Solubility in the IL-rich phase $\pm \sigma$ / ($\text{g}\cdot\text{L}^{-1}$)
CBZ	0.0017 [7]	8.26 \pm 0.60
CAF	21.6 [7]	28.60 \pm 0.27

References

- [1] J.C. Merchuk, Andrews, B.A., Asenjo, J.A., Aqueous two-phase systems for protein separation Studies on phase inversion, *J. Chromatogr. B* 711 (1998) 285-293.
- [2] T.B.V. Dinis, Passos, H., Lima, D.L.D., Esteves, V.I., Coutinho, J.A.P., Freire, M.G., One-step extraction and concentration of estrogens for an adequate monitoring of wastewater using ionic-liquid-based aqueous biphasic systems, *Green Chem.* 17 (2015) 2570-2579.
- [3] M.G. Freire, Cláudio, A.F.M., Araújo, J.M.M., Coutinho, J.A.P., Marrucho, I.M., Canongia Lopes, J.N., Rebelo, L.P.N., Aqueous biphasic systems: a boost brought about by using ionic liquids, *Chem. Soc. Rev.* 41 (2012) 4966-4995.
- [4] K.E. Gutowski, Broker, G.A., Willauer, H.D., Huddleston, J.G., Swatloski, R.P., Holbrey, J.D., Rogers, R.D., Controlling the aqueous miscibility of ionic liquids: Aqueous biphasic systems of water-miscible ionic liquids and water-structuring salts for recycle, metathesis, and separations, *J. Am. Chem. Soc.* 125 (2003) 6632-6633.
- [5] H. Passos, Ferreira, A.R., Cláudio, A.F.M., Coutinho, J.A.P., Freire, M.G., Characterization of aqueous biphasic systems composed of ionic liquids and a citrate-based biodegradable salt, *Biochem. Eng. J.* 67 (2012) 68-76.
- [6] H. Passos, Sousa, A.C.A., Ramiro Pastorinho, M., Nogueira, A.J.A., Rebelo, L.P.N., Coutinho, J.A.P., Freire, M.G., Ionic-liquid-based aqueous biphasic systems for improved detection of bisphenol A in human fluids, *Anal. Methods* 4 (2012) 2664-2667.
- [7] PhysProp Database. <http://srcinc.com/what-we-do/environment.aspx>, 2016 (accessed 22/12/2016).