

Supporting Information

Ionic-Liquid-Based Aqueous Biphasic Systems for Improved Detection of Bisphenol A in Human Fluids

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Experimental Section

Materials. BPA, 4,4'-(propane-2,2-diyl)diphenol, ≥ 99 wt % pure, was from Aldrich. The ionic liquids used in the ABS composition were 1-ethyl-3-methylimidazolium chloride, [C₂mim]Cl (> 98 wt %); 1-butyl-3-methylimidazolium chloride, [C₄mim]Cl (99 wt %); 1-hexyl-3-methylimidazolium chloride, [C₆mim]Cl (> 98 wt %); 1-allyl-3-methylimidazolium chloride, [amim]Cl (> 98 wt %) 1-butyl-1-methylpyrrolidinium chloride, [C₄mpyr]Cl (99 wt %); tetrabutylammonium chloride, [N₄₄₄₄]Cl (≥ 97 wt %); tetrabutylphosphonium chloride, [P₄₄₄₄]Cl (98 wt %); and choline chloride, [N_{1112OH}]Cl (≥ 98 wt %). All ionic liquids were commercially acquired from Iolitec, with the exception of [P₄₄₄₄]Cl that was kindly supplied by Cytec Industries Inc., [N₄₄₄₄]Cl that was from Aldrich and [N_{1112OH}]Cl that was from Sigma. Ionic liquids individual samples were dried under constant conditions before use (at moderate vacuum and temperature and for a minimum of 48 h). The purity of each ionic liquid was further checked by ¹H and ¹³C NMR spectra and found to be in accordance with the purities given by the suppliers. Urea, 99 wt % pure, was supplied by Panreac and was used without further purification. K₃PO₄, 98 wt % pure, and NaCl, 99.9 wt % pure, were from Sigma and Normapur, respectively. The 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 was prepared by the dissolution of urea and NaCl in pure water, at the concentrations of 1.2 g·dm⁻³ and 4.0 g·dm⁻³, respectively.

Experimental Procedure. The solubility curves of [C₄mpyr]Cl, [P₄₄₄₄]Cl, [N₄₄₄₄]Cl and [N_{1112OH}]Cl were determined through the cloud point titration method (previously described by us¹), and at (298 ± 1) K and atmospheric pressure. Aqueous solutions of K₃PO₄ at 50 wt % and aqueous solutions of the different hydrophilic ionic liquids (with concentrations ranging from 60-70 wt %) were prepared and used for the determination of the binodal curves. The binodal curves of the remaining ionic liquids were previously reported by Neves et al.²

The experimental binodal curves were further fitted by the following eq³:

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

where [IL] and [Salt] are the ionic liquid and the inorganic salt mass fraction percentages, respectively, and A, B, and C are constants obtained by the regression of the experimental binodal data.

The tie-lines (TLs) were determined by a gravimetric method originally proposed by Merchuck et al.³ for polymer-based ABS, and later on applied by Rogers and co-workers⁴ to ionic-liquid-based ABS. A ternary mixture composed of ionic liquid + K₃PO₄ + water at the biphasic region was gravimetrically prepared within $\pm 10^{-4}$ g, vigorously agitated, and left to equilibrate for at least 12 h and at (298 ± 1) K, aiming at a complete separation of the coexisting phases. After such time, both phases were carefully separated and individually weighed.

Each TL was determined by the lever-arm rule through the relationship between the top phase composition and the overall system composition, and for which the following system of four equations (eqs 2 – 5) and four unknown values ($[IL]_{IL}$, $[IL]_{Salt}$, $[Salt]_{IL}$ and $[Salt]_{Salt}$) was solved:³

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

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

$$[IL]_{IL} = \frac{[IL]_M}{\alpha} - \frac{1-\alpha}{\alpha} \times [IL]_{Salt} \quad (4)$$

$$[Salt]_{IL} = \frac{[Salt]_M}{\alpha} - \frac{1-\alpha}{\alpha} \times [Salt]_{Salt} \quad (5)$$

where subscripts “IL”, “Salt”, and “M” designate the ionic-liquid-rich phase, the salt-rich phase and the mixture, respectively; $[Salt]$ and $[IL]$ represent, respectively, the weight fractions of K₃PO₄ and ionic liquid; and α is the ratio between the mass of the top phase and the total mass of the mixture. The system solution results in the composition (wt %) of the ionic liquid and inorganic salt in the top and bottom phases.

For the calculation of each tie-line length (TLL) the following equation was used:

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

where subscripts “IL” and “Salt” symbolize, respectively, the ionic-liquid-rich phase and the salt-rich phase, and $[Salt]$ and $[IL]$ are the mass fraction percentages of organic salt and IL, as described before.

The pH values (± 0.02) of the ionic-liquid-rich and inorganic-salt-rich aqueous phases were measured at (298 ± 1) K using an HI 9321 Microprocessor pH meter (HANNA instruments). The compositions adopted at the biphasic region are the same as those applied for the TLs determination and BPA partitioning studies.

For fixed ternary compositions, and for which the TLs were previously determined, new biphasic systems were prepared making use of an aqueous solution of BPA at 4.3×10^{-4}

$\text{mol}\cdot\text{dm}^{-3}$ instead of pure water. Each mixture was gravimetrically prepared within $\pm 10^{-4}$ g, vigorously agitated, and left to equilibrate for at least 12 h and at (298 ± 1) K, aiming at a complete partitioning of BPA. Equilibrations studies confirmed that the complete partitioning of BPA among the phases was attained after 6 h. After 12 h of equilibration, both phases were carefully separated, individually weighed, and used for the BPA quantification and confirmation of the TLs compositions.

The BPA quantification, in both phases, was carried out by UV spectroscopy using a SHIMADZU UV-1700, Pharma-Spec spectrometer, at a wavelength of 293 nm, and using a calibration curve previously established in alkaline medium (above the pKa of BPA). Possible interferences of both the inorganic salt and the ionic liquid with the analytical method were taken into account and blank controls were always employed.

The stability of BPA in the coexisting phases of all systems was confirmed and it is safe to admit that the molecule is stable at least up to 72 h in the ABS media.

Results

The phase diagrams determined in this work are depicted in Figure S1. Moreover, Figure S1 also presents the graphical representation of each TL which corresponds to the mixture used for the partitioning studies of BPA. Figure S2 shows the phase diagrams of $[\text{C}_2\text{mim}]\text{Cl}$, $[\text{C}_4\text{mim}]\text{Cl}$, $[\text{C}_6\text{mim}]\text{Cl}$ and $[\text{amim}]\text{Cl}$ containing systems and respective TLs. Figures S3 and S4 show the diverse mixture compositions evaluated for the extraction of BPA from aqueous phases with $[\text{C}_2\text{mim}]\text{Cl}$ - and $[\text{N}_{1112}\text{OH}]\text{Cl}$ -based systems.

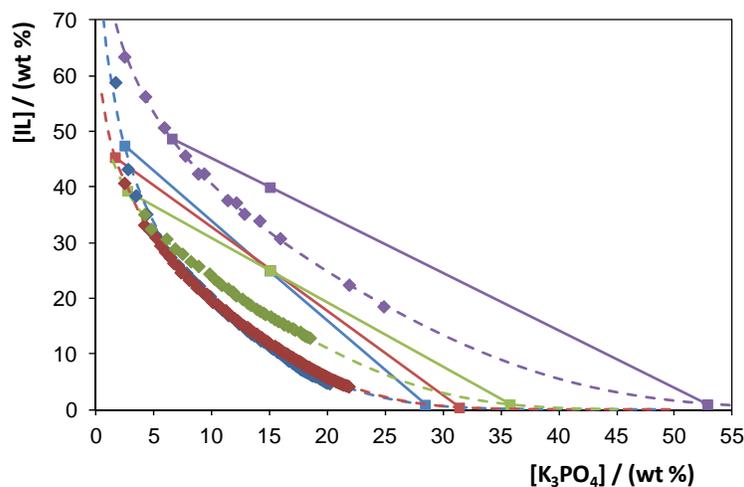


Fig. S1. Phase diagrams for ABS composed of ionic liquid + water + K_3PO_4 : (\blacklozenge) $[C_4mpyr]Cl$, (\blacklozenge) $[P_{4444}]Cl$, (\blacklozenge) $[N_{4444}]Cl$, (\blacklozenge) $[N_{11120H}]Cl$, (\blacksquare) TL data, (--) fitted curve by eq (1). The colour of each TL and fitted curve correspond to the same colour of the respective phase diagram.

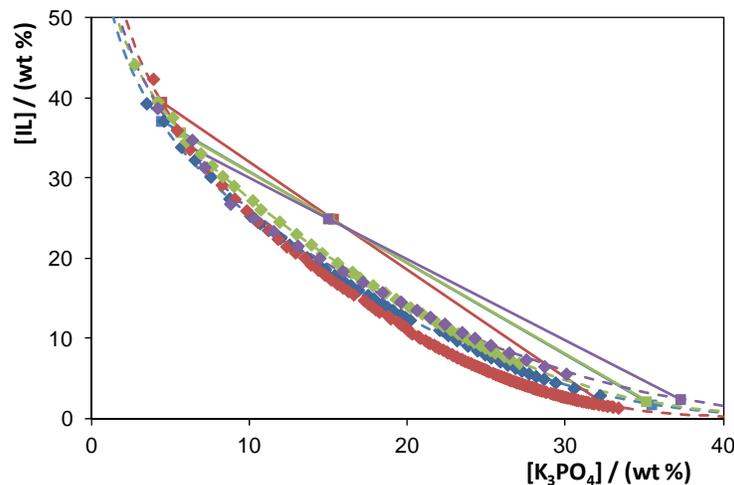


Fig. S2. Phase diagrams for ABS composed of ionic liquid + water + K_3PO_4 : (\blacklozenge) $[C_2mim]Cl$, (\blacklozenge) $[C_4mim]Cl$, (\blacklozenge) $[C_6mim]Cl$, (\blacklozenge) $[amim]Cl$, (\blacksquare) TL data, (--) fitted curve by eq (1). The colour of each TL and fitted curve correspond to the same colour of the respective phase diagram.

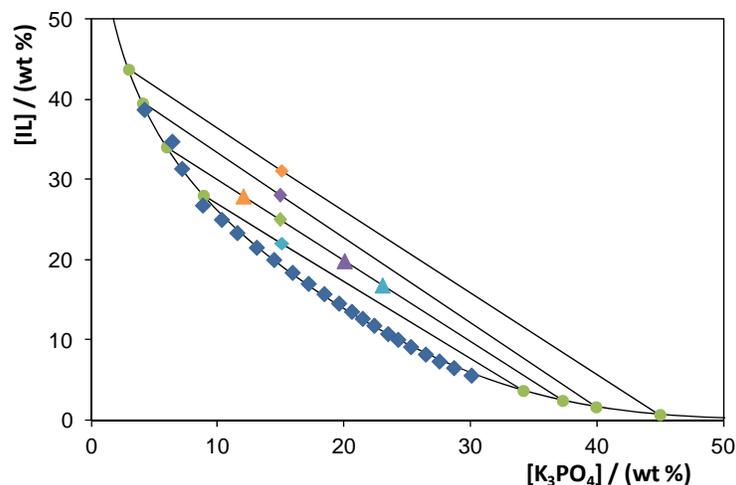


Fig. S3. Phase diagrams for the $[C_2mim]Cl + K_3PO_4$ ABS: (\blacklozenge) binodal curve data; (—) fitted curve by eq (1); (\bullet) TL data; extraction points: (\blacktriangle) 12.00 wt % of K_3PO_4 + 27.94 wt % of IL; (\blacktriangle) 20.00 wt % of K_3PO_4 + 19.87 wt % of IL; (\blacktriangle) 23.00 wt % of K_3PO_4 + 16.84 wt % of IL; (\blacklozenge) 15.00 wt % of K_3PO_4 + 22.00 wt % of IL; (\blacklozenge) 15.00 wt % of K_3PO_4 + 25.00 wt % of IL; (\blacklozenge) 15.00 wt % of K_3PO_4 + 28.00 wt % of IL; and (\blacklozenge) 15.00 wt % of K_3PO_4 + 31.00 wt % of IL.

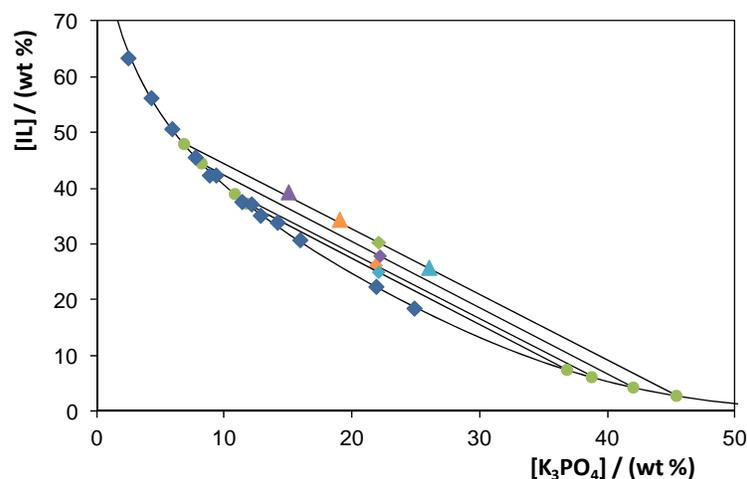


Fig. S4. Phase diagrams for the $[N_{1112OH}]Cl + K_3PO_4$ ABS: (\blacklozenge) binodal curve data; (—) fitted curve by eq (1); (\bullet) TL data; extraction points: (\blacktriangle) 15.00 wt % of K_3PO_4 + 40.00 wt % of IL; (\blacktriangle) 19.00 wt % of K_3PO_4 + 34.47 wt % of IL; (\blacktriangle) 26.00 wt % of K_3PO_4 + 25.85 wt % of IL; (\blacklozenge) 22.00 wt % of K_3PO_4 + 25.00 wt % of IL; (\blacklozenge) 22.00 wt % of K_3PO_4 + 26.00 wt % of IL; (\blacklozenge) 22.00 wt % of K_3PO_4 + 28.00 wt % of IL; and (\blacklozenge) 22.00 wt % of K_3PO_4 + 30.77 wt % of IL.

Table S1 presents the detailed extraction efficiencies of BPA obtained with the several systems investigated, the mixture compositions (and respective tie-lines and tie-line lengths), and the pH of the coexisting phases. Table S2 presents similar information for the urine-type ABS.

Table S1. Extraction efficiencies of BPA (*EE%*) in ionic-liquid-based ABS, mixture compositions, and respective tie-lines (TLs) and tie-line lengths (TLLs), and pH values of the coexisting phases.

| Ionic liquid | weight fraction percentage / wt % | | | | | | | | TLL | <i>EE%</i> ± 0.2 |
|--------------------------|-----------------------------------|-------------------------------|------------------|----------------------------|------------------------------|-------------------------------|---------------------------------|--------------------|--------|---------------------|
| | [<i>IL</i>] _{IL} | [<i>Salt</i>] _{IL} | pH _{IL} | [<i>IL</i>] _M | [<i>Salt</i>] _M | [<i>IL</i>] _{Salt} | [<i>Salt</i>] _{Salt} | pH _{Salt} | | |
| [C ₂ mim]Cl | 28.027 | 8.848 | 13.18 | 21.994 | 15.117 | 3.690 | 34.139 | 13.09 | 35.100 | 99.4 |
| | 34.059 | 5.943 | 13.13 | 24.956 | 14.959 | 2.450 | 37.251 | 13.18 | 44.630 | 99.8 |
| | 39.516 | 4.043 | 13.32 | 27.973 | 14.975 | 1.656 | 39.899 | 13.04 | 52.144 | 100.0 |
| | 43.730 | 2.941 | 13.28 | 31.018 | 15.079 | 0.694 | 44.958 | 13.63 | 60.146 | 100.0 |
| [C ₄ mim]Cl | 37.110 | 4.401 | 13.05 | 25.016 | 15.022 | 1.788 | 35.421 | 12.97 | 47.009 | 99.5 |
| [C ₆ mim]Cl | 39.513 | 4.427 | 12.93 | 24.938 | 15.290 | 1.637 | 32.657 | 12.92 | 47.239 | 99.1 |
| [amim]Cl | 35.734 | 5.622 | 13.25 | 25.028 | 15.021 | 2.183 | 35.077 | 13.24 | 44.647 | 99.9 |
| [C ₄ mpyr]Cl | 39.322 | 2.714 | 13.40 | 25.028 | 15.026 | 0.971 | 35.748 | 13.07 | 50.617 | 98.5 |
| [P ₄₄₄₄]Cl | 47.450 | 2.471 | 13.04 | 24.978 | 14.992 | 0.897 | 28.414 | 12.69 | 53.296 | 99.1 |
| [N _{1112OH}]Cl | 45.359 | 1.644 | 13.37 | 25.077 | 15.051 | 0.380 | 31.378 | 13.11 | 53.918 | 99.3 |
| | 37.365 | 11.706 | 13.11 | 25.035 | 22.074 | 7.546 | 36.779 | 12.99 | 38.959 | 98.9 |
| | 39.089 | 10.780 | 13.14 | 26.024 | 21.887 | 6.230 | 38.715 | 13.00 | 43.129 | 99.6 |
| | 44.572 | 8.183 | 13.18 | 27.949 | 22.153 | 4.370 | 41.966 | 13.01 | 52.512 | 100.0 |
| | 48.838 | 6.516 | 13.25 | 30.740 | 22.124 | 2.470 | 46.505 | 12.22 | 61.230 | 100.0 |

Table S2. Extraction efficiencies of BPA ($EE\%$) in urine-type ionic-liquid-based ABS and respective mixture compositions.

| Ionic liquid | weight fraction percentage / wt % | | $EE\% \pm 0.2$ |
|------------------|-----------------------------------|------------|----------------|
| | $[IL]_M$ | $[Salt]_M$ | |
| $[C_2mim]Cl$ | 24.977 | 14.994 | 99.8 |
| $[C_4mim]Cl$ | 25.049 | 15.195 | 100.0 |
| $[C_6mim]Cl$ | 25.053 | 15.007 | 99.6 |
| $[amim]Cl$ | 25.064 | 15.104 | 100.0 |
| $[C_4mpyr]Cl$ | 25.012 | 15.024 | 99.9 |
| $[P_{4444}]Cl$ | 25.038 | 14.994 | 98.9 |
| $[N_{4444}]Cl$ | 24.994 | 14.901 | 100.0 |
| $[N_{1112OH}]Cl$ | 40.026 | 14.850 | 100.0 |

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