Supplementary information: Facilitated solvent screening for membrane-based extraction of chiral amines via a priori simulations

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SD-1 Molecular structures of the cations

Figure 1. Molecular structures of the considered cations.
SD-2 Molecular structures of the anions

![Molecular structures of the considered anions.](image)

*Figure 2. Molecular structures of the considered anions.*
SD-3 Wetting profile of a porous substrate

A typical wetting profile is given in Figure 3. The apparent contact angle was determined by drawing the tangent to the curve in region (d)-(f), in which a slower decline of the contact angle is visible. Then, the intersection of this tangent is taken with the y-axis.

Figure 3. Schematic representation of the wetting process of a droplet on a porous substrate, based on Han et al. [1]
SD-4 Analysis of critical solvent parameters

SD-4.1 COSMO-RS accuracy

Figure 4. Simulated density plotted versus the experimental density of fourteen RTILs at 30 °C.

Figure 5. Simulated viscosity plotted versus the experimental viscosity of fourteen RTILs at 30 °C.
Figure 6. Simulated water solubility plotted versus the experimental water solubility of thirteen RTILs at 30 °C.

Figure 7. Simulated ionic liquid solubility in water plotted versus the experimental ionic liquid solubility in water of fourteen RTILs at 30 °C.
Figure 8. Phase miscibility range of fourteen RTILs. Positive and negative values represent the solubility of water in the IL and vice versa, respectively.
SD-5 $\sigma$-surfaces and profiles of the considered cations

- [C4mim]$^+$
- [C6mim]$^+$
- [Amim]$^+$
- [C4vim]$^+$
- [MeOCH2CH2-mim]$^+$
- [Bzmim]$^+$
- [C3mpy]$^+$
- [C4mpy]$^+$
- [C3mPyr]$^+$
- [S2,2,2]$^+$
Figure 9. $\sigma$-profiles and $\sigma$-surfaces of all the considered cations.

SD-6 $\sigma$-surfaces and profiles of the considered anions

Figure 10. $\sigma$-profiles and $\sigma$-surfaces of all the considered anions.
SD-7 $\sigma$-surfaces and profiles of the considered ionic liquids
Figure 11. ς-profiles and ς-surfaces of all the considered ionic liquids. The ionic liquids are (a) [C4mim][PF6], (b) [C4mim][N(Tf)2], (c) [C4mim][C(CN)3], (d) [C4mim][BETI], (e) [P6,6,6,14][N(Tf)2], (f) [C3mPyr][N(Tf)2], (g) [C6mim][N(Tf)2], (h) [C4mpy][N(Tf)2], (i) [Amim][N(Tf)2], (j) [Bzmim][N(Tf)2], (k) [C3mpy][N(Tf)2], (l) [MeOCH2CH2-mim][N(Tf)2], (m) [S2,2,2][N(Tf)2], (n) [C4vim][N(Tf)2], (o) [N8,8,8,1][Cl].

SD-8 ς-profiles of the considered solutes

Figure 12. ς-profiles of MBA, MPPA and IPA.
SD-9 Box plot analysis of the IL-wettability of porous polymeric substrates

Figure 13. Box plots of the contact angle of ILs on four polymeric porous substrates for varying anions (left) and cations (right).
SD-10 Hansen Solubility Parameter approach and results for the shortlist extractants

The Hansen solubility parameters (HSPs) are based on the assumption that the binding or cohesion energy $E$ of a compound can be written as the sum of three contributions, due to nonpolar, dipolar and hydrogen bonding interactions:

$$E = E_D + E_P + E_H$$

Other sources of cohesion energy can be defined as well, such as induced dipoles, metallic bonds, etc., but the previous ones are the major types found in organic molecules. By dividing each contribution by the molar volume $V_M$, the squared Hildebrand solubility parameter $\delta_T$ can be written as the sum of the squared HSPs:

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$

The SI units for these parameters are MPa$^{1/2}$. In principle, chemical compounds with similar HSPs will show physical affinities. The distance $D$ between the HSPs of the solvent and the solute is defined by Hansen and Skaarup (with solute = 1 and solvent = 2):

$$D^2 = 4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2$$

Experimentally, the HSP coordinates can be calculated by analysing the compound miscibility in solvents with known HSPs $[2], [3]$. To this end, 17 standard solvents were used for the solubility tests of the ionic liquids, i.e., 1-butanol, 1,4-dioxane, acetone, aniline, benzyl alcohol, $N,N$-dimethylformamide, DMSO, ethanol, ethanolamine, ethylene glycol, formamide, $\gamma$-butyrolactone, methanol, $n$-hexane, $N$-methylformamide, $N,N$-dimethylacetamide and toluene. The solubility tests consisted of the mixing of the ionic liquid with a standard solvent and observing visually if phase separation (= 0) or full miscibility (= 1) occurred. By plotting the HSPs of all the standard solvents and indicating the solubility behaviour (= 0 or 1), an HSP-plot can be made to determine the hydrophobicity of the considered IL. The results for the shortlist ionic liquids, namely $[P6,6,6,14][N(Tf)2]$, $[C3mPyr][N(Tf)2]$, $[C6mim][N(Tf)2]$ and $[S2,2,2][N(Tf)2]$, are given in Figure 14.

![Figure 14. Hansen Solubility Parameters plots of the ionic liquids, (a) $[P6,6,6,14][N(Tf)2]$, (b) $[C3mPyr][N(Tf)2]$ and (c) $[C6mim][N(Tf)2]$ and $[S2,2,2][N(Tf)2]$.](image-url)
SD-11 Emulsion testing of the shortlist extractants

The emulsification of the shortlist ionic liquids in aqueous phases was tested as follows. First, an emulsion was prepared by adding three droplets of the ionic liquid in 6 mL of MilliQ-water in a tube. Second, the tubes were shaken by hand to initiate the emulsification and immersed in an ultrasonic bath for 45 minutes. The samples were then inserted in a Turbiscan Classic MA2000 (Formulaction) to measure the transmission and backscattering. The sampling was done immediately after ultrasonication and after 1, 3, 6, 24, 48 and 120 hours. The transmission results of undecane, Aliquat-336, [P6,6,6,14][N(Tf)2] and [C6mim][N(Tf)2] are given in Figure 15.

Figure 15. Transmission results for four solvents after 0, 1, 3, 6, 24, 48 and 120 hours after emulsification.
The fluxes of solute $i$ (MBA or MPPA) for the ME-experiments were determined as follows:

$$J_i = \frac{(C_f(t_1) - C_f(t_2))}{(t_2 - t_1)} \frac{V}{A_{\text{eff}}} \frac{g}{m^2h}$$

in which $C_f(t)$ is the feed concentration of the solute at time $t$ [g/L], $V$ is the feed volume [L] and $A_{\text{eff}}$ is the effective membrane surface area [m$^2$]. The membrane surface area was equal to 0.000561 m$^2$. The feed volume is assumed to be constant at 250 mL over 24 hours, as the loss due to sampling is considered negligible. The times $t_1$ and $t_2$ are time points in between which the flux has stabilised.

For example, the MBA-flux was calculated by determining the time points $t_1$ and $t_2$ based on Figure 16, after which the formula above was used. For the experiment using undecane, $t_1 = 1$ h and $t_2 = 6$ h, whilst for the experiment at 50 °C using the ionic liquid, $t_1 = 1$ h and $t_2 = 24$ h.

![Figure 16. MBA-flux calculation procedure. The data points at 30, 40 and 50 °C were retrieved from the experiments using the ionic liquid as the extractant.](image-url)
Figure 17. The simulated and experimental viscosity of [P6,6,6,14][N(Tf)2] as a function of temperature.
References

