## Supporting information

The electrochemical stability and the effect of alkyl chain of the imidazolium cation in the polarization limits of pure ionic liquids was established by cyclic voltammograms shown in Figure S1 and measured at the Hg/imidazolium pure liquids interfaces at 303 K. The three imidazolium ionic liquids under study were 1 - ethyl - 3 - methylimidazolium bis(trifluoromethylsulfonyl)imide, [C<sub>2</sub>MIM][Tf<sub>2</sub>N], 1 - hexyl - 3 - methylimidazolium bis(trifluoromethylsulfonyl)imide, [C<sub>6</sub>MIM][Tf<sub>2</sub>N] and 1 - dodecyl - 3 - methylimidazolium bis(trifluoromethylsulfonyl)imide, [C<sub>12</sub>MIM][Tf<sub>2</sub>N].



Figure S1 - Cyclic voltammograms measured at Hg/imidazolium pure liquids interfaces at 303  $\pm$  2 K.

Figures S2 and S3 show the comparison of cyclic voltammograms measured at the Hg/ionic liquid binary mixtures interface ( $[C_6MIM][Tf_2N] + [C_{12}MIM][Tf_2N]$  and  $[C_2MIM][Tf_2N] + [C_{12}MIM][Tf_2N]$  respectively) with different molar ratios and with a scan rate of 50 mV.s<sup>-1</sup>. The cathodic limit for these mixtures is practically independent of the mole fraction when the second component is liquid [ $C_{12}MIM$ ][ $Tf_2N$ ].



Figure S2 - Cyclic voltammograms measured at Hg/[C<sub>6</sub>MIM][Tf<sub>2</sub>N] + [C<sub>12</sub>MIM][Tf<sub>2</sub>N] interfaces at  $303 \pm 2$  K.



Figure S3 - Cyclic voltammograms measured at Hg/[C<sub>2</sub>MIM][Tf<sub>2</sub>N] + [C<sub>12</sub>MIM][Tf<sub>2</sub>N] interfaces at  $303 \pm 2$  K.