Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for Effects of Dilution in Ionic Liquid Supercapacitors

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Locating the SSCS Transition

The second-order λ-line in the phase diagram in Fig. 3 was calculated by stepping the bulk volume fraction from low to high, and identifying the volume fraction where the surface charge becomes finite. This process is done for various α below the tri-critical point. The continuous SSCS transition is shown in Fig. S1.

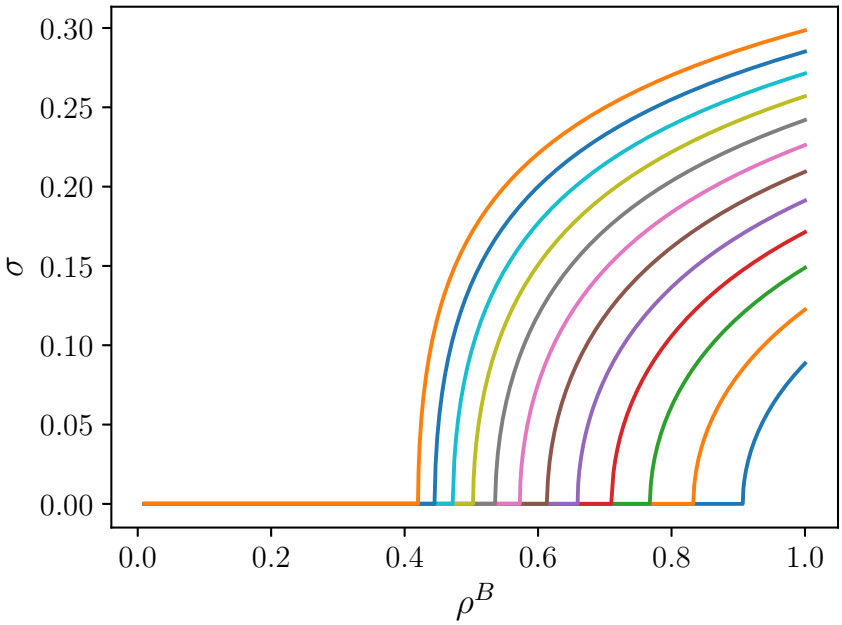

Figure S1 Surface charge vs. bulk concentration for $0.26 < \alpha < 0.4$, which is below the tri-critical point. The curves are ordered by their α value which is decreasing from left to right. Note that the second-order transition from disordered to surface charge separated is continuous.

The binodal, disordered spinodal, and SSCS spinodal are found by analyzing the Ω–μ plot for various α above the tri-critical point. The free energy curve for the disordered state at a given α is calculated by stepping the bulk volume fraction from low to high starting from a homogeneous state. The free energy curve for the SSCS state is calculated by stepping the bulk volume fraction from high to low starting from a charge separated state. The spinodal of each state is the limit

of stability, where thermodynamic stability is defined as $\partial^2\Omega/\partial\mu^2 < 0$. The coexistence point is where the separate free energy curves cross. At this point $\mu^I = \mu^{II}$ and $\Omega^I = \Omega^{II}$ where I and II represent the disordered and SSCS states, respectively. The Ω–μ plot for $\alpha = 0.8$ is given in Fig. S2.

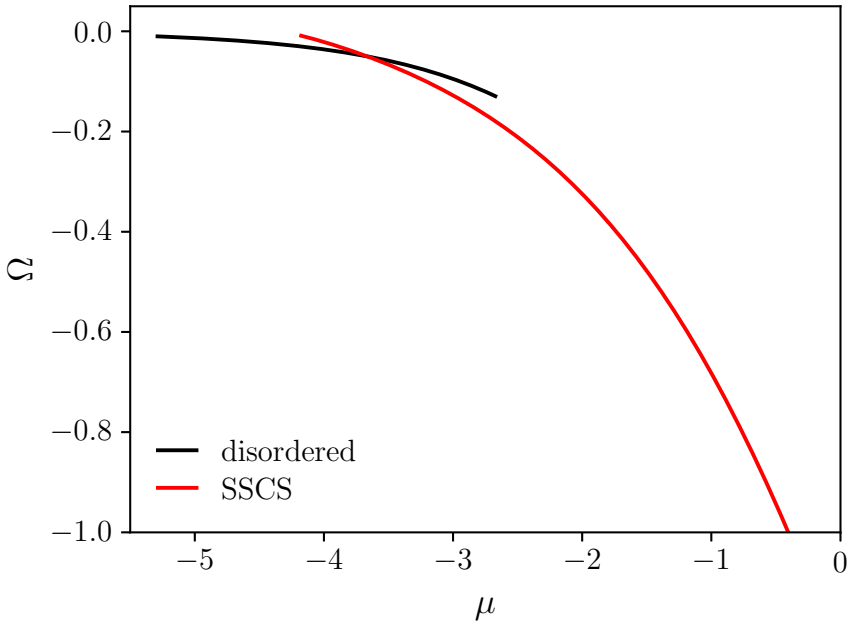

Figure S2 Free energy vs. chemical potential for $\alpha = 0.8$. Note that $\alpha = 0.8$ is above the tri-critical point. Metastable regions are regions that obey $\partial^2\Omega/\partial\mu^2 < 0$ but are not the lowest free energy states. Once a spinodal is reached, the system jumps to the stable branch.

The location of the two spinodals was also confirmed by observing the surface charge. Starting from a near homogeneous state and stepping the chemical potential up while calculating the equilibrium charge and potential profiles at each step, the spinodal of the disordered (homogeneous) phase is reached at the first instance where a finite surface charge is observed. A finite surface charge indicates that the system has charge separated and is no longer disordered. Similarly, starting from a charge separated state and stepping the ion concentration (or chemical potential) down while calculating the charge and potential profiles at each step, the ordered spinodal is reached at the first instance where a zero surface charge is observed.

$\alpha = 0$ Results

The results for $\alpha = 0$ are presented to serve as a comparison to the finite α cases highlighted in the main text. In the $\alpha = 0$ case, the model without preferential adsorption reduces to the model developed by Kornyshev.[1]

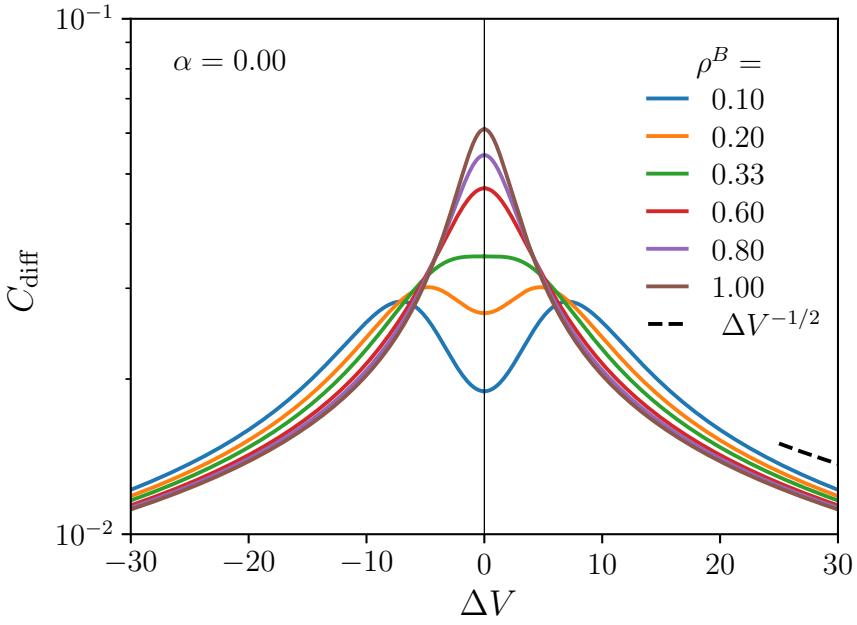

Figure S3 C_{diff} vs ΔV plotted for RTILs with varying dilution at $\alpha = 0$. Note the transition from bell to camel-shaped curves at $\rho^B = 1/3$ (green).

Notes and references

1 A. A. Kornyshev, *J. Phys. Chem. B*, 2007, **111**, 5545–5557.