Supplementary Information for "Effects of Surface Transition and Adsorption on Ionic Liquid Capacitors"

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The critical point for spontaneous charge separation

In the absence of preferential adsorption (i.e. $h = 0$) and applied voltage, we can analytically derive the critical condition for the spontaneous surface charge separation by performing a linear stability analysis. We consider an ionic liquid in contact with a planar metal plate at $z = 0$ and coupled to a large bath of the ionic liquid at $z = +\infty$. We assume a small surface charge σ, and expand the free energy to quadratic order in all the field variables. Variation of the free energy yields a set of linear equations for these field variables. Substitution of the solutions back into the free energy results in a quadratic function in σ. The critical condition is reached when the quadratic coefficient vanishes. The set of linear differential equations to

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solve for the three fields are.

$$\phi + \tilde{\sigma}\delta(\tilde{z}) = -2\tilde{\lambda}_D^2\tilde{\nabla}^2\psi \tag{S.1}$$

$$\phi = 2\tilde{\lambda}_D^2(\tilde{\nabla}^2 Y - Y)/\alpha \tag{S.2}$$

$$\phi = -(\psi + Y), \tag{S.3}$$

with the boundary conditions,

$$2\tilde{\lambda}_D^2\tilde{\nabla}\psi|_{\tilde{z}} = -\tilde{\sigma} \tag{S.4}$$

$$\tilde{\nabla}Y|_{\tilde{z}=0} = 0 \tag{S.5}$$

$$\int_0^{+\infty} \psi d\tilde{z} = \tilde{\sigma} - \frac{\tilde{\sigma}\alpha}{2\tilde{\lambda}_D^2} \tag{S.6}$$

$$\int_0^{+\infty} Y d\tilde{z} = \frac{\tilde{\sigma}\alpha}{2\tilde{\lambda}_D^2}. \tag{S.7}$$

Here we scale all the lengths by the electrostatic correlation length, l_c. This set of ODE has the following oscillatory solutions for the three fields,

$$
\begin{aligned}
\psi &= \left[\frac{\tilde{\sigma}(1 - \frac{\alpha}{2\tilde{\lambda}_D^2})(k_1^2 + k_2^2)}{2k_2} - \frac{\tilde{\sigma}}{4\tilde{\lambda}_D^2 k_2}\right] e^{-k_1\tilde{z}}\sin(k_2\tilde{z}) \\
&\quad + \left[\frac{\tilde{\sigma}(1 - \frac{\alpha}{2\tilde{\lambda}_D^2})(k_1^2 + k_2^2)}{2k_1} + \frac{\tilde{\sigma}}{4\tilde{\lambda}_D^2 k_1}\right] e^{-k_1\tilde{z}}\cos(k_2\tilde{z}), \tag{S.8}
\end{aligned}
$$

$$
Y = \frac{\tilde{\sigma}\frac{\alpha}{2\tilde{\lambda}_D^2}(k_1^2 + k_2^2)}{2k_2}e^{-k_1\tilde{z}}\sin(k_2\tilde{z}) + \frac{\tilde{\sigma}\frac{\alpha}{2\tilde{\lambda}_D^2}(k_1^2 + k_2^2)}{2k_1}e^{-k_1\tilde{z}}\cos(k_1\tilde{z}), \tag{S.9}
$$

$$
\begin{aligned}
\phi &= \left[\frac{\tilde{\sigma}}{4\tilde{\lambda}_D^2 k_2} - \frac{\tilde{\sigma}(k_1^2 + k_2^2)}{2k_2}\right] e^{-k_1\tilde{z}}\sin(k_2\tilde{z}) \\
&\quad - \left[\frac{\tilde{\sigma}}{4\tilde{\lambda}_D^2 k_1} + \frac{\tilde{\sigma}(k_1^2 + k_2^2)}{2k_1}\right] e^{-k_1\tilde{z}}\cos(k_2\tilde{z}). \tag{S.10}
\end{aligned}
$$

The wave numbers k_1 and k_2 here have the following form,

$$k_1 = C^{1/2}\cos(\theta/2), \ k_2 = C^{1/2}\sin(\theta/2), \tag{S.11}$$

where $C = \sqrt{\frac{1}{2\tilde{\lambda}_D^2}}$ and $\tan\theta = \frac{|(\alpha - 2\tilde{\lambda}_D^2 - 1)^2 - 8\tilde{\lambda}_D^2|^{1/2}}{2\tilde{\lambda}_D^2 + 1 - \alpha}$. Substituting the solutions back into the free energy, we can solve for $\alpha_{s,c}$ when the second derivative $\frac{\partial^2(\mathcal{F})}{\partial\tilde{\sigma}^2}$ vanishes. This yields the critical condition for the spontaneous charge separation transition,

$$\alpha_{s,c} = 2\tilde{\lambda}_D^2 + \sqrt{2}\tilde{\lambda}_D. \tag{S.12}$$

Fitting for real ionic liquids

To map real ionic liquids onto the phase digram of our model, we need to find values of the four parameters for each ionic liquid, which include the ion volume (v), the permittivity (ϵ), the electrostatic correlation length (l_c), and the correlation strength (α). The electrostatic correlation length is approximated as the ion size in the fitting, $l_c = b$.

For molten NaCl, we use the data sets from the MD studies[1,2] where ions are modeled as Lennard-Jones (LJ) particles with Coulomb interactions. The parameter b and v are determined according to the diameter and the density of LJ particles used in the MD study. Vacuum permittivity ϵ is assumed for NaCl. The parameter α is fitted by matching the peak intensity in $S(\mathbf{k})$ from our model to that from the MD study. The charge-density structure factor $S(\mathbf{k})$ from the fitted model is shown and compared with that from the MD study in Fig. S1a.

For the two imidazolium-based RTILs, we used molar concentration data from the MD studies[3,4] to obtain the ion volume v. Then by assuming random close packing of sphere with packing fraction at 0.63, we obtain the ion size b from $b^3 = 0.63(6/\pi)v$. The values of permittivity for the two RTIL are obtained from an experimental study.[5] Finally, the parameter α is fitted by matching the peak intensity in $S(\mathbf{k})$ from our model to that from

the two MD studies. $S(\mathbf{k})$ from the fitted models for the two imidazolium-based RTILs are shown alongside with that from the fitted molten NaCl model in Fig. S1b.
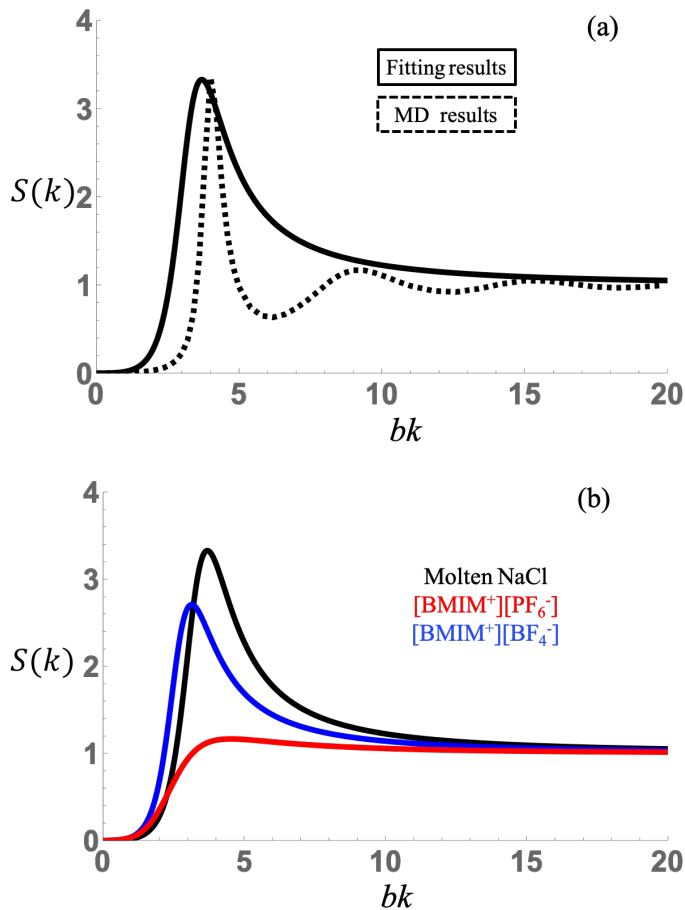

Figure S1: Charge-density structure factors. (a) The structure factor, $S(\mathbf{k})$, from the fitted model for molten NaCl (solid line) and the MD study (dashed line). (a) The structure factor, $S(\mathbf{k})$, from the fitted models for Molten NaCl (black), $[\text{BMIM}^+][\text{PF}_6^-]$ (red), and $[\text{BMIM}^+][\text{BF}_4^-]$ (black).

Critical condition for asymmetric adsorption

To see how the critical value $\alpha_{s,c}$ and $\Delta V_{s,c}$ behave with changes in the adsorption strength, h, for the asymmetric case, we perform a similar linear stability analysis. However, with the form of the half-sided harmonic potential, the equations cannot be solved analytically. In Fig. S2, we plot $\alpha_{s,c}$ and $\Delta V_{s,c}$ as functions of h, obtained from numerical calculations

corresponding to the setting in Fig. 1 of the main text, with a large enough separation. The critical α increases slightly from 0.17 to 0.19 and shows a nonlinear relationship with increasing h. The corresponding ΔV curve is linear with h at small h but starts to deviate from linearity when h becomes large ($h > 5$). The nonlinearity indicates that the potential difference ΔV cannot be simply mapped to an adsorption energy except in the linear regime.
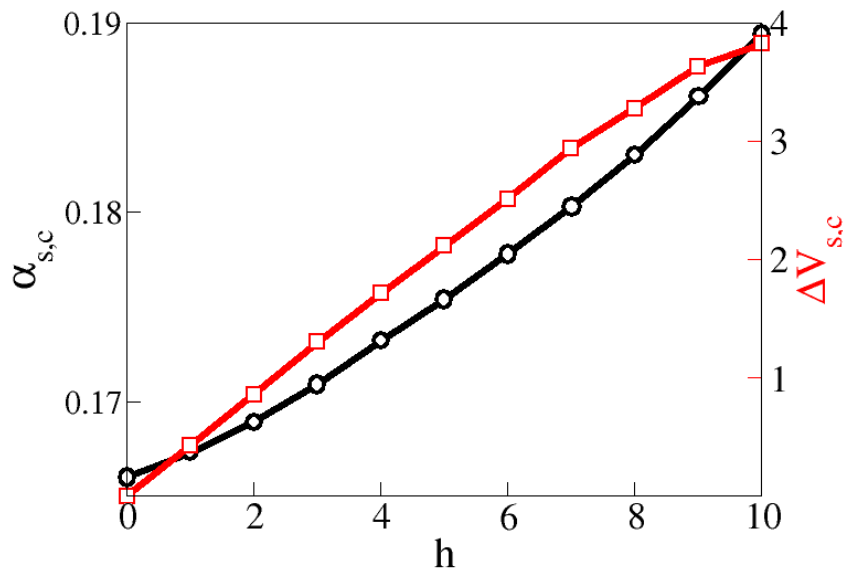

Figure S2: $\alpha_{s,c}$ (black line with circles, left axis) and $\Delta V_{s,c}$ (red line with squares, right axis) are plotted as function of the asymmetric adsorption strength $h_2 = h$ with $\lambda_D = 0.1b$.

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