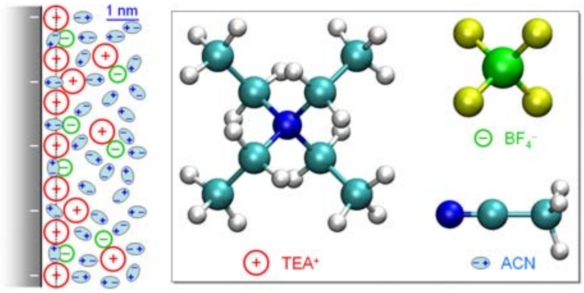
Supplementary Material (ESI) for *PCCP*

Structure and Dynamics of Electrical Double Layers in Organic Electrolytes†

Guang Feng,[a] Jingsong Huang,[b] Bobby G. Sumpter,[b] Vincent Meunier[b] and Rui Qiao[a]*



Graphical contents entry: A molecular view of the electrical double layer in an organic electrolyte of tetraethylammonium cation and tetrafluoroborate anion in acetonitrile.

[a] *College of Engineering & Science, Clemson University, Clemson, South Carolina, 29634-0921, USA. Tel: 864-656-5627. Fax: 864-656-4435. Email: rqiao@clemson.edu. URL: http://www.clemson.edu/~rqiao*

[b] *Oak Ridge National Laboratory, Bethel Valley Road, Oak Ridge, Tennessee 37831-6367, USA.*

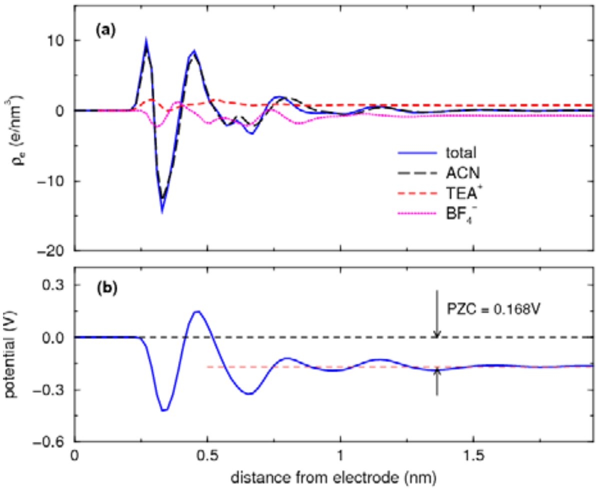


Figure S1. (a) Space charge density of ACN molecules, TEA$^+$ cations and BF$_4^-$ anions. (b) Electrostatic potential distribution near a neutral electrode.

Charge separation and electrical potential distribution of the EDLs were studied for the electrodes at potential of zero charge. The space charge density profiles were computed from a MD trajectory and the electrical potential distribution was obtained by solving Poisson equation with the space charge density as input. Figures S1a and S1b show the space charge density and the electrical potential distribution near the electrode. Although the alternating ion layers (see Figure 4b) suggest that there may be significant charge separation near the electrode, a careful examination of the space charge density near the electrode (see Figure S1a) shows that the space charge density due to the TEA$^+$ and BF$_4^-$ ions largely cancels each other out in the 0.3−1.0 nm region. This is mainly due to the fact that, unlike simple ions such as Na$^+$ and Cl$^-$, the net charge of complex organic ions is distributed among their multiple atoms rather than localized at their center of mass. Further examination of the space charge density profiles in Figure S1a indicates the local space charge density is dominated by the ACN molecules at most locations. The non-zero local space charge due to ACN molecules is caused by their preferential orientation near the electrode. Overall, a small potential difference of 168 mV develops between the electrode and the bulk electrolyte, which represents the potential of zero charge (PZC) of the electrode/electrolyte system studied here.

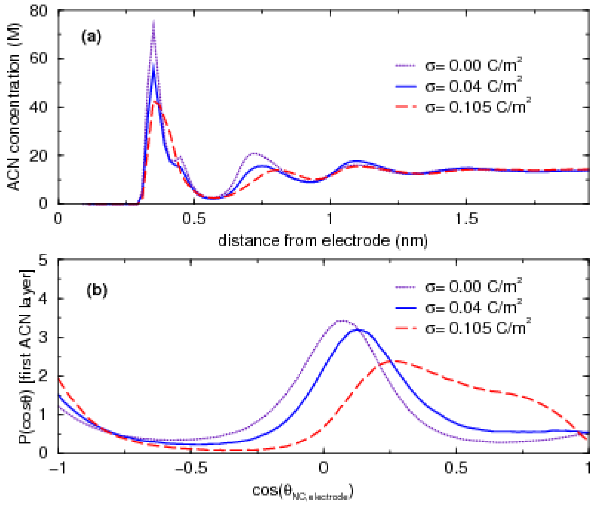


Figure S2. (a) Concentration distribution of ACN molecules near electrodes with various charge densities, (b) Orientation distribution of the NC vector (defined in the caption of Fig. 3) of ACN molecules within 0.56nm of the electrode with respect to the normal direction of electrodes.

For positive electrodes, the evolution of the ACN concentration profile near the electrode as the magnitude of electrode charge density increases is similar to that observed near the negative electrode (Figure 8). However, in contrast to the EDLs near negative electrodes (Figure 8), when the electrode charge density becomes more positive, the NC vectors of the interfacial ACN molecules become more aligned with the normal direction of the electrode.