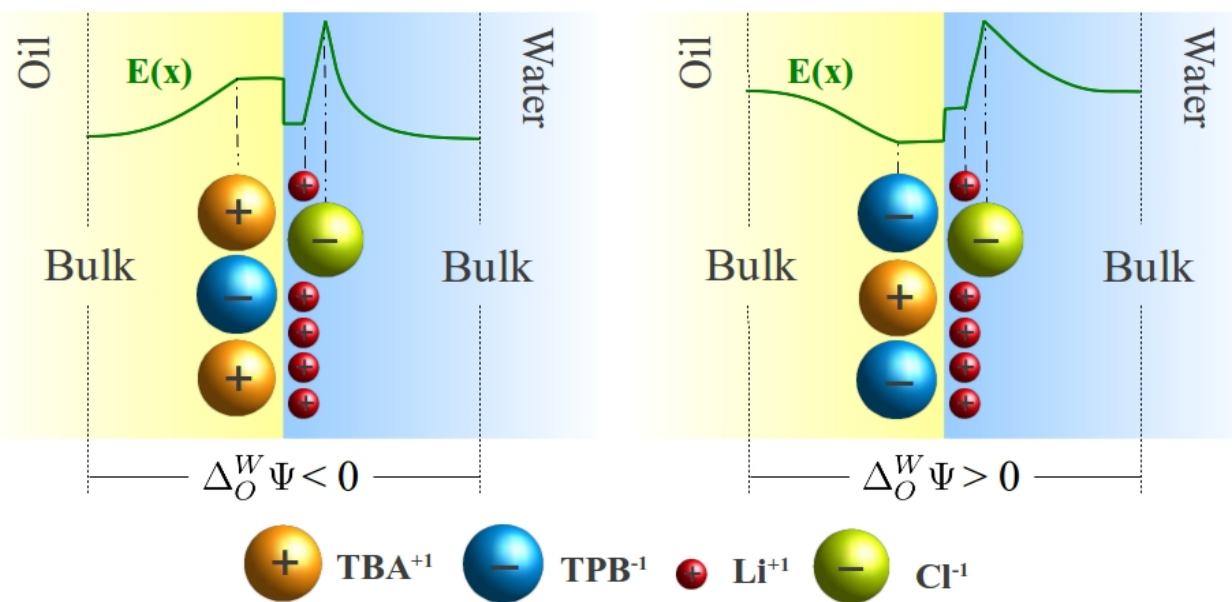


Enhancing and reversing the electric field at the oil/water interface with size-asymmetric monovalent ions

Guillermo Iván Guerrero-García, Yufei Jing, and Monica Olvera de la Cruz
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We performed Monte Carlo simulations of an experimental oil/water interface in the presence of an electric field including a realistic ionic size-asymmetry, ion correlations, excluded volume of ions, and image charges to study the surface tension of oil/water interfaces in the presence of size asymmetric monovalent salts with the goal of determining the effects of ion correlations, polarization, and ionic excluded volume in the diffuse electrical double layer. At the molecular level, we observe that the electrolyte concentration and the ionic size-asymmetry can be used to tune the electric field near the liquid/liquid interface. We also reproduce surface tension experimental data of LiCl and TBATPB near an oil/water interface in the presence of an electric field, contrasting with the results of the classical non-linear Poisson-Boltzmann theory.



Here, we show that the ionic size-asymmetry between small cations and large anions can significantly increase or reverse locally the electric field near a liquid-liquid interface at high salt concentrations. This suggests a robust ionic trapping/release mechanism at oil-water interfaces in the vicinity of the point of zero charge.