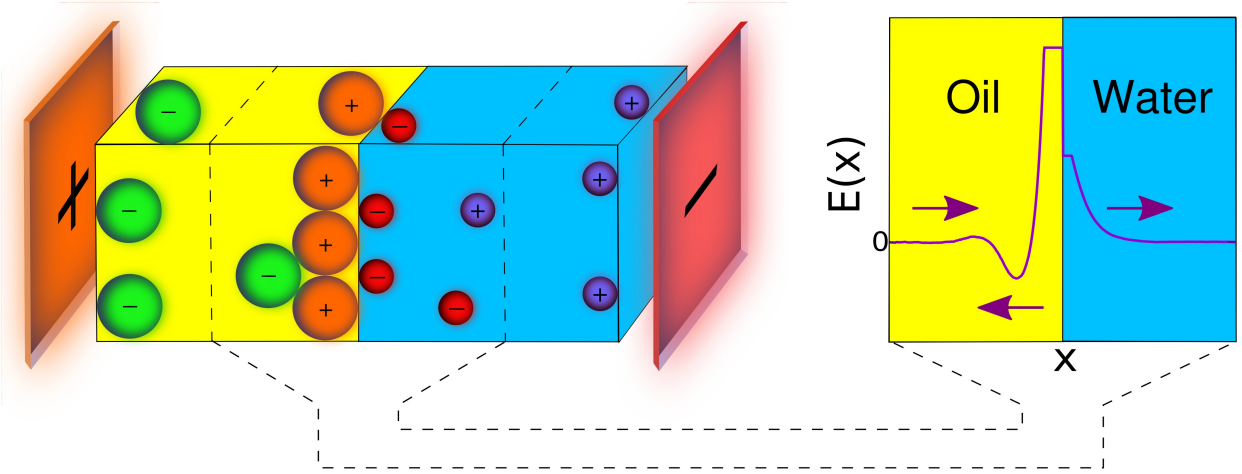
Inversion of the electric field at the electrified liquid-liquid interface

Guillermo Iván Guerrero-García and Mónica Olvera de la Cruz
Department of Materials Science & Engineering, Northwestern University, Evanston, IL, USA

The thermodynamics of the general system of two immiscible electrolytes in the presence of an electric field depends strongly on the distribution of ions near the liquid interface. Here, we calculate the corresponding electrostatic potential difference, excess surface tension, and differential capacity via Monte Carlo simulations, which include ion correlations and polarization effects for equally sized ions in water, and equally sized ions in oil.



At high salt concentrations, charge overcompensation in the lower-permittivity region is observed, which results in a local inversion of the electric field accompanied by charge inversion near the interface. In addition, our Monte Carlo simulations predict that the differential capacity is maximal at the point of zero charge, in contrast with the classical Poisson-Boltzmann theory results.

Guerrero-García and Olvera de la Cruz, J. Chem. Theory Comput. (Letter), DOI: http://dx.doi.org/10.1021/ct300673m

NSF MRSEC award No DMR-1121262 and AFOSR Award FA9550-10-1-0167

MRSEC