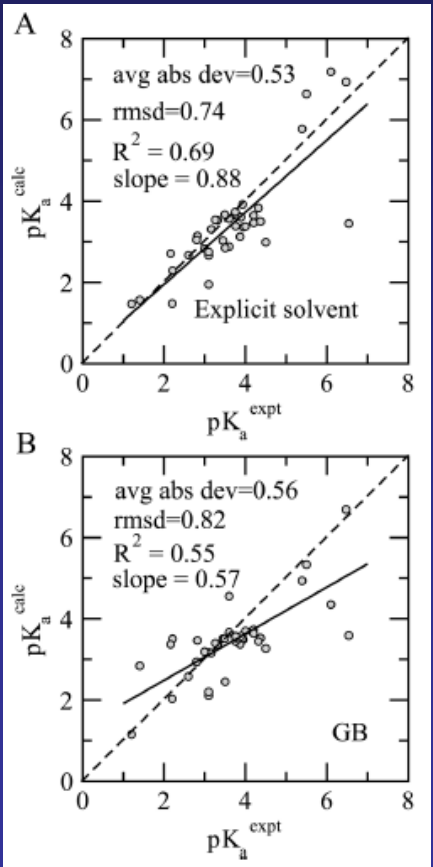
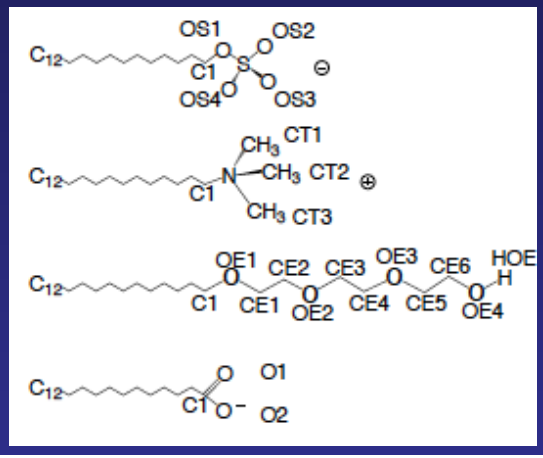
Probing Regular Solution Theory for Mixed Amphoteric/Ionic Surfactant Systems by Molecular Dynamics Simulations

Jana K. Shen, Department of Chemistry & Biochemistry, University of Oklahoma

The goal of this PRF funded project is to develop and apply a new method based on molecular dynamics simulations to for mechanistic studies of pH-dependent properties of surfactant assemblies. In the second grant year, we extended the continuous constant pH molecular dynamics (CpHMD) technique to explicit-solvent simulations. We applied the new technique in conjunction with a generalized Born (GB) model that was parameterized in the first grant year to predict and dissect the microscopic origins of the pK_a shifts of a single surfactant solubilized in ionic and nonionic micelles, which is of interest in detergent industry and oil refinery processes. The results of this work are being summarized in two manuscripts with two graduate students as the first authors.

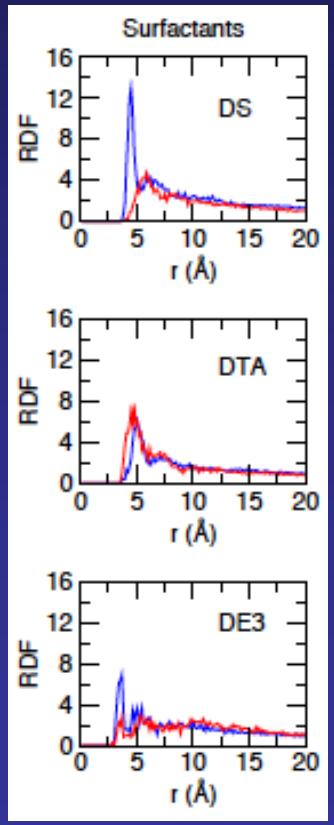


Comparison of calculated and experimental pK_a's using CpHMD simulations in explicit- and GB-solvent.



Micelle	Implicit solvent[a] 0.15 M	Explicit solvent[a] 0.15 M	Explicit solvent[a] 0 M	Experiment[b]
DS	2.5±0.33	3.2±0.02	5.3	2.8±0.1 (SDS) 2.8±0.1 (LiDS)
DTA	-3.0±0.06	1.5±0.01	0.6	0.1±0.1 (DTAC) 0.9±0.1 (DTAB)
DE3	1.6±0.26	1.7±0.09	1.5	1.9±0.1 (DE8)

Predicted pK_a's of lauric acid in three micelles using CpHMD simulations in explicit- and GB-solvent.



Radial distribution functions showing the interaction between the lauric acid and micellar surfactant headgroups.