Thermodynamics of Ternary Electrolytes: Enhanced Adsorption of Macroions as Minority Component at Liquid Interfaces

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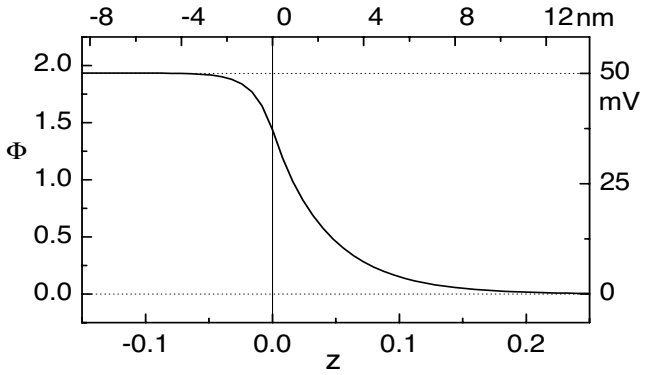
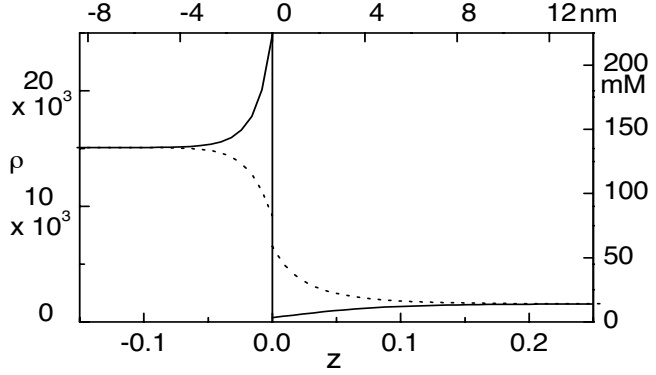
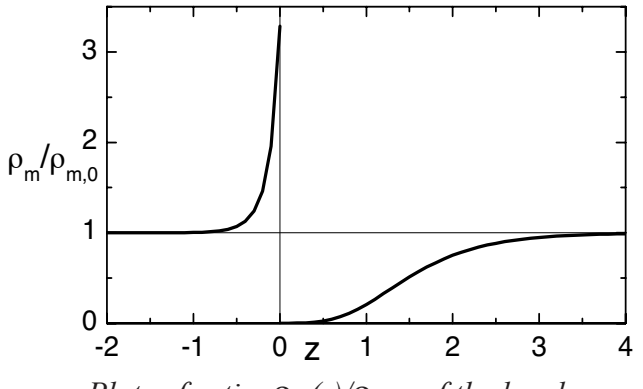
We study the equilibrium thermodynamics between two ternary ionic systems in immiscible solvents characterized by different dielectric constants. We consider system geometries wherein the two phases of immiscible solvents occupy, respectively, semi-infinite regions of space separated by neutral and charged planar interfaces. Specifically, we analyze the case where the ternary system is composed of a pair of symmetric ions plus a minority charged component of high valence. Our main result consists of first obtaining exact analytical solutions, within a nonlinear mean-field description, of the electrostatic potentials as well as density profiles for the underlying binary ionic system and extending these results to the the ternary case using perturbation theory. We show that the corresponding adsorption and depletion of macroions of multivalency at the interface are highly enhanced when compared with the monovalent counterparts.



Plot of the electrostatic potential for the system of a membrane separating the two chemically distinct regions with different salt concentrations, similar to those found in physiological systems. The distribution potential Φ_D is 1.93 in dimensionless units (50 mV); dimensionless and mV scales are shown at left and right sides of the above plot, respectively. The horizontal scale is shown in dimensionless units at bottom, and in nanometers on top.



Plots the number density of ions in a system separating two regions with different salt concentrations, similar to those found in physiological systems. The concentration of positive ions is shown in a solid line, and for negative ions in a dotted line. Dimensionless and mM scales are shown at left and right. The horizontal scale is shown in dimensionless units at bottom of the plot and in units of nanometers on the top.



Plots of ratio, $\rho_m(z)/\rho_{m,0}$, of the local minority component particle density to the bulk density value. The minority components has a valence of $Z_m=10$. In the infinitely-dilute limit, this minority charged component acts as a perturbation to a theoretical NaCl-nitrobenzene/water base system with $\Phi_D=0.99$, $\varepsilon_w=80.0$, $\varepsilon_n=37.9$, and a neutral interface. Note that in the vicinity of the interface, in the less polar phase in the region of $z>0$, the particle density is highly suppressed.