The impact of water on the local electric potential of spherical ionic micelles by MD simulation

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The most commonly used theoretical approach to analyze the electric double layer (EDL) properties is the Poisson-Boltzmann (PB) theory. In this theory, the assumption of a structureless solvent of constant dielectric permittivity and representation of ions as point charges are used. This theory describes fairly well the EDL capacitance and potential in simple cases. However, application of the PB theory for complex systems, particularly with multi-charged ions and/or nonuniformly charged surfaces, appears to be an unjustified simplification. The major problem is to estimate the contribution of polar solvent to the EDL properties, i.e., the unknown local dependence of the solvent dielectric permittivity in the non-uniform electric field. Molecular dynamics (MD) and Monte Carlo methods make it possible to study the effect of solvent polarization on the EDL. Though simulations are time-consuming, they give the precise value of a local field as soon as the molecular models have been chosen.

Ionic micelles in an aqueous solution containing single-charged counter-ions have been simulated by molecular dynamics. For both cationic and anionic micelles, it has been demonstrated that explicit description of solvent has strong effect on the micelle's electric field. We investigate several models of water differing in the number of interacting centers, the distribution of charges on these centers and the rigidity of this charge distribution (unpolarizable/polarizable model) (SPC, TIP5P, two-centered [1], and polarizable SWM4-NDP [2]). The water models used are characterized by similar dipole moment values though they differ by the spatial arrangement of the effective charged centers. Besides, they have different values of multipole moments relative to the oxygen atom. For four molecular models of water, the results have been compared with those for the continuum solvent model.

The results of simulation show that the continuum model of polar solvents does not give relevant description of the EDL even in the presence of singly charged counter-ions. The electric potential calculated with the aid of continuum solvent model is substantially overestimated outside micellar crown and underestimated inside the crown. The continuum solvent model gives considerably slower spatial decay of the electric potential than the molecular models of water. Spatial separation of effective charges in the water molecule and the magnitude of these charges are the major source of differences in the electric potentials calculated from the continuum model and from the molecular models. The larger is the distance between positive and negative charges the more considerable is the effect of the explicit solvent. The asymmetry of water molecules leads to the differences in the structure of EDL for anionic and cationic micelles. The major differences are observed in the micellar crown that controls the structure of the rest of EDL.

[1] K. M. Dyer, J. S. Perkyns, G. Stell, and B. M. Pettitt, *Mol. Phys.*, 2009, 107, 423.
[2] G. Lamoureux, E. Harder, I. V. Vorobyov, B. Roux, and A. D. MacKerell, Jr. Chem. Phys. Lett., 2006, 418, 245.