Steric effects on the dynamics of electrolytes MUSTAFA SABRI
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Paris, France. — The classical Poisson-Boltzmann (PB) theory of electrolytes as-
sumes a dilute solution of point charges with mean-field electrostatics. Even for very
dilute solutions, however, it predicts absurdly large ion concentrations (exceeding
close packing) for surface potentials of only a few tenths of a volt. In this talk,
we adopt a simple model for steric effects with only one parameter (the effective
ion size), and we analyze the charging of a thin double layer, which must form a
condensed layer of close-packed ions near the surface at high voltage. A surprising
prediction is that the differential capacitance varies non-monotonically with the ap-
plied voltage, and thus so does the response time of an electrolytic system. This
effect is able to predict the reversal of AC electro-osmotic flow at high voltage and
high frequency, as well as the increase of capacitance with temperature in molten
salts.

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