

## Failures of Linearized Poisson Boltzmann

The general view is stated by George Stell and C.G. Joslin, The Donnan Equilibrium: A Theoretical Study of the Effects of Interionic Forces. *Biophys J*, 1986. 50(5): p. 855-859.

“Under physiologically appropriate conditions, we find that it is almost never valid to use Debye-Huckel theory to calculate ionic activities: it is important to take proper account of ion size.”

The view is stated by Torrie and Valleau *Journal of Physical Chemistry*, 1982: 86: 3251-3257

“It is immediately apparent that Classical Theory has Broken Down completely. It .... fails to show [the] qualitative behavior [and] is seriously in Error for quite low concentrations and charges”

“When the counterions are doubly charged ... the Classical Theory Fails Altogether even for quite low concentrations and charges”

The paper of Fraenkel Simplified electrostatic model for the thermodynamic excess potentials of binary strong electrolyte solutions with size-dissimilar ions. *Molecular Physics*, 2010. 108(11): p. 1435 - 1466. is a good recent reference.

The books of Zemaitis, J.F. and Pytkowicz, R.M. (see below) are classical compilations of experimental data and theoretical models that attempt to deal with the issues just quoted. Kontogeorgis, G.M. and G.K. Folas is the most recent compilation I know of.

The following references are numerous but are still a small subset of what has been done on this very subject.

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