Modelling steric finite size effects in the electric double layer of electrolytes and ionic liquids at electrode surfaces

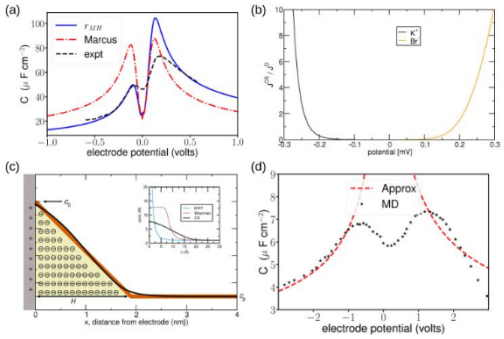
Drew Parsons[a], Dagmawi B. Tadesse[b], Matteo Farci[a]

[a] Department of Chemical and Geological Sciences and CSGI, University of Cagliari, Cittadella Universitaria, S.S. 554 bivio Sestu, Monserrato, 09042, CA, Italy
[b] School of Engineering and Energy, Murdoch University, 90 South Street, Murdoch, 6150, WA, Australia

drew.parsons@unica.it

DLVO theory was constructed to describe interactions between charged surfaces with relatively low surface potentials, 5-50 mV, or 0.2-2 kT in thermal energy. But electrochemical systems typically involve potentials 0.3-3V, or 10-100 kT. At such potentials it is indispensable to include steric forces due to finite ion size in theoretical models [1]. In modified Poisson-Boltzmann modelling steric effects introduce a concentration cap to counterion adsorption profiles, the effect of which is to introduce a maximum in the electrode capacitance as electrode potential increases [2], see Figure 1a. The steric effect starts to dominate when the electrode potential reaches 200 mV relative to bulk solution. The same is true in nonequilibrium systems where electric current is flowing: Poisson-Nernst-Planck (drift-diffusion) models must be modified to include the steric force, and the corresponding steric flux exceeds the diffusion flux (both arising from concentration gradients, distinct from drift current due to the electric field) when the potential exceeds 0.2V, see Figure 1b.
In conventional low-potential conditions the counterion adsorption profile (electric double layer) follows an exponential profile. Curiously, under steric conditions above 200 mV, we observe an approximately linear profile, Figure 1c, when applying the well-regarded Carnahan-Starling model of the steric force. The steric concentration
cap is not reached until much higher potentials above 4V. The approximation of a linear profile enables construction of a semianalytical model [3], which might be used in place of the Grahame equation to relate surface potential to surface charge.
Combined with a Clausius-Mossotti description of the permittivity of the electric double layer, this approximation may be successfully applied to both aqueous electrolytes, Fig.1b, and ionic liquids Fig.1d, the region of validity being the steric regime above 200 mV. The theory will be useful for understanding electrocatalysis in ionic liquids, and improving electrodes for energy storage or electroosmosis.

Keywords:
electrochemical surface, steric force, finite ion size, electrolyte theory



(a) Capacitance of Ag in 0.1M NaF, exp (black), semianal. approximation, various ion radii (red, blue) (b) Ratio of steric to diffusion flux at various potentials. (c) Linear counterion steric concentration profile. (d) Capacitance in EMIM-TFSI ionic liquid, MD (black) and semianal. approx (red).

References:

[1] Drew F. Parsons, Matteo Farci, Alin Grigoras, and Dagmawi Tadesse. Ch.9 in The FEniCS Project, Simula SpringerBriefs on Computing 19, 2026. https://doi.org/10.1007/978-3-032-17396-6_9
[2] Dagmawi B. Tadesse, Drew F. Parsons. Colloids and Surfaces A: Physicochemical and Engineering Aspects 648 (2022) 129134. https://doi.org/10.1016/j.colsurfa.2022.129134
[3] Dagmawi B. Tadesse, Drew F. Parsons. Electrochimica Acta 531 (2025) 146266. https://doi.org/10.1016/j.electacta.2025.146266