
--Electronic Supplementary Information--

Dmitry Momotenko,\textsuperscript{a} Carlos M. Pereira\textsuperscript{b} and Hubert H. Girault\textsuperscript{a,\ast}.

\textsuperscript{a} Laboratoire d’Electrochimie Physique et Analytique, Ecole Polytechnique Fédérale de Lausanne, Station 6, CH-1015 Lausanne, Switzerland

\textsuperscript{b} CIQ-UP L4, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

\ast CORRESPONDING AUTHOR FOOTNOTE

EMAIL: hubert.girault@epfl.ch

Telephone number: +41-21-693 3145

Fax number: +41-21-693 3667
SI-1. Simulation details

The numerical modelling was performed by solving coupled Nernst-Planck and Poisson equations within a one dimensional computational domain using "Nernst-Planck without electroneutrality" and "Poisson equation" modes from COMSOL Multiphysics (version 3.5a). The computational domain was divided into two subdomains, representing aqueous and organic phases respectively. A set of Nernst-Planck equations were established in each subdomain in such way that ions could not permeate through liquid/liquid boundary. The value of relative permittivity given by sigmoidal function was specified in the Poisson equation application mode that was set over the whole computational domain. The numerical resolution of equations system was performed in a parametric way using direct solver UMFPACK taking the bias value V0 as a parameter. The mesh size was refined down to $10^{-14}$ m which is sufficient enough to avoid inaccuracy attributed to the mesh size. All the constant values, expressions, mesh details subdomain and boundary conditions used in simulations are shown in the COMSOL report file. It is also important to note that values of diffusion coefficients of corresponding ionic species have no influence on the numerical result.


The classical formulation of Gouy-Chapman case for ITIES assume the bulk values of relative permittivity in each phase, i.e. neglecting smooth change of solvent properties at the interphase. Therefore, the bulk values of relative permittivity were set for each corresponding subdomain and the differential capacitance was evaluated as follows

$$C_d = \pm \frac{\partial}{\partial s}(f_s - f_\infty)$$

while calculating surface charge density at the interface as the subdomain integral of space charge density, i.e.

$$= \int F \cdot z_i \varepsilon_i$$
Figure S-1 shows the very good correlation between numerical and analytical result for the calculated Gouy-Chapman capacitance at ITIES

\[
C_d / \mu F cm^{-2}
\]

Figure S-1. Differential capacitance curves at the water/DCE interface containing 1:1 electrolyte at bulk concentration of 1 mM calculated within frameworks of Gouy-Chapman theory. Numerical and analytical results are represented as dots and continuous red line, respectively.

**SI-3. Nernst-Planck formulation taking into account ion solvation effect**

The flux of species \( i \) could be written as

\[
J_i = \frac{D_i}{RT} c_i \nabla_i
\]

where \( \mu_i \) denote the chemical potential of species \( i \) and, considering activity of the ion to be equal to concentration like in case of infinite dilution, could be considered as follows

\[
\mu_i = \mu_i^0 + RT \ln c_i + z_i F
\]

Therefore, the flux equation reads

\[
J_i = \frac{D_i}{RT} c_i \nabla_i \mu_i^0 + \frac{z_i F}{RT} D_i c_i \nabla_i
\]

The term in squared brackets is the normal form of Nernst-Planck equation describing ionic flux arising from diffusion and migration transport processes. At the same time, taking into account ion solvation in accordance with Born theory we can write

\[
\mu_i^0 = \frac{z_i^2 e^2 N_a}{8 \rho_i} \left( \frac{1}{r} \right)
\]
where $e$, $N_a$ and $r_{\text{ion}}$ denote elementary charge, Avogadro constant and ionic radius, respectively.

Therefore, the flux equation reads

$$J_i = \frac{D_i}{RT} c_i \frac{z_i^2 e^2 N_a}{8} \frac{\nabla}{r} \left[ D_i \nabla c_i + \frac{z_i F}{RT} D_i c_i \nabla \right]$$

In Nernst-Planck application mode the equations system for each subdomain is formulated as

$$\nabla\left( D_i \nabla c_i \frac{z_i F}{RT} D_i c_i \nabla \right) = R \ u \nabla c_i$$

In such a way we can define $R$ and $u$ terms by differentiating first solvation term in the flux equation.

Hence, the total formulation could be rewritten

$$\nabla\left( D_i \nabla c_i \frac{z_i F}{RT} D_i c_i \nabla \right) = \frac{z_i^2 e^2 N_a}{8} \frac{D_i}{\theta'_{\text{ion}} RT} \left( \nabla \left( \frac{\nabla}{r} \right) \frac{2(\nabla r)^2}{r} \right) c_i + \frac{z_i^2 e^2 N_a}{8} \frac{D_i}{\theta'_{\text{ion}} RT} \frac{\nabla}{r}^2 \nabla c_i$$

However, the contribution to the total flux from the ion-solvation effect remains minor and therefore do not change significantly the capacitive behavior of ITIES.