

# Differential capacitance of liquid/liquid interfaces of finite thicknesses: a finite element study.

## --Electronic Supplementary Information--

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**RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required  
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## 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  $V_0$  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.

## SI-2. Gouy-Chapman capacitance and model validation.

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

$$C_d = \pm \frac{q_s}{q(f^s - f^{\infty})}$$

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

$$S = \int F \sum_i z_i c_i$$

Figure S-1 shows the very good correlation between numerical and analytical result for the calculated Gouy-Chapman capacitance at ITIES

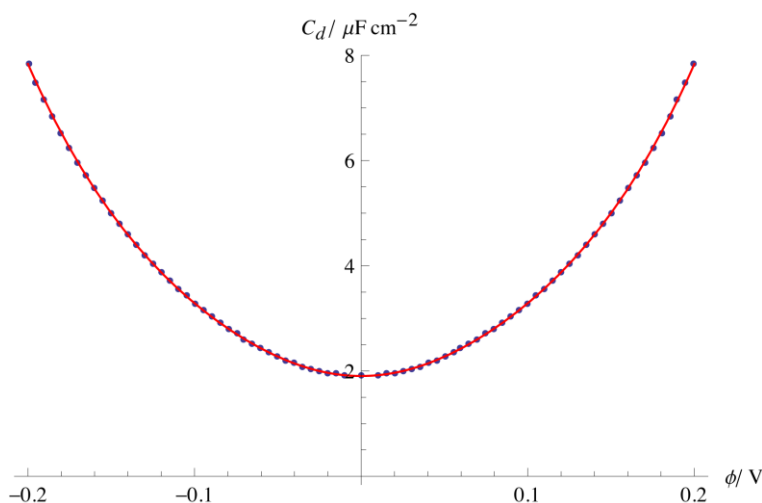


Figure S-1. Differential capacitance curves at the water/DCE interface containing 1:1 electrolyte at bulk concentration of 1 mM calculated within frameworks of Gouy-Chapman theory. Numerical and analytical results are represented as dots and continuous red line, respectively.

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

The flux of species  $i$  could be written as

$$J_i = -\frac{D_i}{RT} c_i \nabla m_i$$

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

$$m_i = m_i^0 + RT \ln c_i + z_i F \phi$$

Therefore, the flux equation reads

$$J_i = -\frac{D_i}{RT} c_i \nabla m_i^0 - \left[ D_i \nabla c_i + \frac{z_i F}{RT} D_i c_i \nabla \phi \right]$$

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

$$m_i^0 = \frac{z_i^2 e^2 N_a}{8 \rho e_0 r_{ion}} \left( \frac{1}{\epsilon_r} - 1 \right)$$

where  $e$ ,  $N_a$  and  $r_{ion}$  denote elementary charge, Avogadro constant and ionic radius, respectively.

Therefore, the flux equation reads

$$J_i = \frac{D_i}{RT} c_i \frac{z_i^2 e^2 N_a}{8 \rho e_0 r_{ion}} \frac{\nabla e_r}{e_r^2} - \left[ D_i \nabla c_i + \frac{z_i F}{RT} D_i c_i \nabla f \right]$$

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

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

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

$$\nabla \left( -D_i \nabla c_i - \frac{z_i F}{RT} D_i c_i \nabla f \right) = \frac{z_i^2 e^2 N_a}{8 \rho e_0 r_{ion}} \frac{D_i}{RT} \left( \frac{\nabla(\nabla e_r)}{e_r^2} - \frac{2(\nabla e_r)^2}{e_r^3} \right) c_i + \frac{z_i^2 e^2 N_a}{8 \rho e_0 r_{ion}} \frac{D_i}{RT} \frac{\nabla e_r}{e_r^2} \nabla c_i$$

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.