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A mixture theory of electrolytes containing solvation effects

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Abstract

In this work we present a new mixture theory of a liquid solvent containing completely dissociated ions to study the space charge layer of electrolytes in contact with some inert metal. We incorporate solvation shell effects (i) in our derivation of the mixing entropy and (ii) in the pressure model. Chemical potentials of ions and solvent molecules in the incompressible limit are then derived from a free energy function. For the thermodynamic equilibrium the coupled equation system of mass and momentum balance, the incompressibility constraint and the Poisson equation are summarized. With that we study the space charge layer of the electrolytic solution for an applied half cell potential and compare our results to historic and recent interpretations of the double layer in liquid electrolytes. The novelties of the new model are: (i) coupling of momentum- and mass-balance equations, (ii) calculation of entropic contributions due to solvated ions and (iii) the potential and pressure dependence of the free charge density in equilibrium.

1 Introduction

First theoretical investigations of the space charge layer in electrolytic solutions date back around 100 years to the work of L. Gouy[8], D. Chapman[4] and O. Stern[13], who extend the original idea of Helmholtz that the electrochemical interface is basically a simple capacitor. The picture drawn from that time stated a charge layer which exponentially decays (diffuse layer) in addition to an *adsorption* layer (Stern layer). Grahame's profound measurements[9] on the capacity of the double layer, which were in disagreement to the commonly accepted theory at that time, gave the hint to Bikerman[1] in 1942 that the Boltzmann distribution ($n_\alpha \propto \mathrm{e}^{-z_\alpha \varphi(x)}$) is inappropriate, as no volumetric effects of the ions are considered. Even though he was the first who extended the double layer model with respect to volumetric restrictions (steric effect), however, he was not able to reconstruct the measured capacities of Grahame and his model was not recognized widely. All modeling efforts at that time had in common that the species densities n_α were *heuristically* modeled as function of the electrostatic potential φ, in order to obtain an explicit representation of the free charge density $q = q(\varphi)$. The space charge layer was then obtained by solving the (non-linear) Poisson-equation

$$\mathrm{div}\ (\varepsilon_0(1+\chi)\nabla\varphi) = -q(\varphi). \tag{1}$$

The theoretical description of electrolytic solutions tended towards coupled Poisson–Nernst–Planck equation systems, which, in equilibrium, also lead to explicit representations $q = q(\varphi)$. The main difference, however, is that such representations are now derived from free energy functions, which describe the respective material. Borukhov *et. al* stated 1997 a free energy[3] which incorporates ion size effects in their entropy of mixing and consequently derived a relation

$q = q(\varphi)$, for which the Poisson equation gave qualitative *satisfactory* results. However, their main parameter a (ion radius) was quite arbitrary set to 1nm.

Nevertheless, almost all continuum mechanical approaches to model the space charge layer in real electrolytic solutions start with some *a priori* knowledge of its actual structure, which is then used to *tailor* a specific model for the desired problem. In contrast, a consistent formulation of a material model for liquid electrolytes should be able to predict the structure of the double layer, *i.e.* the decomposition of the Stern-layer and the diffuse layer, as function of the applied potential.

In this letter we show that the application of non-equilibrium thermodynamics, and its rational coupling to electrodynamics[12, 5], naturally reveals the pressure p and the electric potential φ as independent variables. We derive a free energy function which embodies solvation effects of the dissociated ions, in additional to mechanical stress and calculate the chemical potentials of all constituents in the incompressible limit. We further show that eq. (1) is only a special case of generic coupled equation system

$$\text{div } (\varepsilon_0(1+\chi)\nabla\varphi) = -q(\varphi, p) \tag{2}$$

$$\nabla p = -q(\varphi, p)\,\nabla\varphi, \tag{3}$$

which self consistently computes φ and the pressure p.

With this model we are able to propose the actual structure of the space charge region in electrolytic solutions and study its decomposition in diffuse and Stern layer regions, as function of the applied potential. The resulting concentrations of ions in the charge layer are physically meaningful and the charge stored in the double layer is in agreement with experimental data.

2 Configurational entropy

Consider a mixture of $\mathcal{N}_0$ solvent molecules and $\mathcal{N}_\alpha, \alpha = 1, \dots, N$ ions (with charge number z_α and mass m_α), with the total number of particles $\mathcal{N} = \sum_{\alpha=0}^{N} \mathcal{N}_\alpha$. Classically it is assumed that **all** particles of the mixture may exchange, leading to the number W^{Boltz} of micro-states as

$$W^{\text{Boltz}} = \binom{\mathcal{N}}{\mathcal{N}_0, \mathcal{N}_1, \dots, \mathcal{N}_N}. \tag{4}$$

In contrast, we consider a mixture in which some of the solvent molecules are *bounded* to the ions, forming solvated cations and anions[11]. Hence, the $\mathcal{N}_0$ solvent molecules split into $\mathcal{N}_0^F$ *free* solvent molecules and $\mathcal{N}_0^B$ bounded solvent molecules,

$$\mathcal{N}_0 = \mathcal{N}_0^F + \mathcal{N}_0^B. \tag{5}$$

Each ion of constituent α is assumed to bound κ_α solvent molecules, and thus $\mathcal{N}_0^B = \sum_{\alpha=1}^{N} \kappa_\alpha \mathcal{N}_\alpha$. The exchange of a particle in the solvation shell with a free solvent molecule is thus **not** an admissible permutation (*c.f.* FIG 1). The number of (entropically) exchangeable particles $\tilde{\mathcal{N}}$ is hence

$$\tilde{\mathcal{N}} = \mathcal{N}_0^F + \textstyle\sum_{\alpha=1}^{N} \mathcal{N}_\alpha, \tag{6}$$

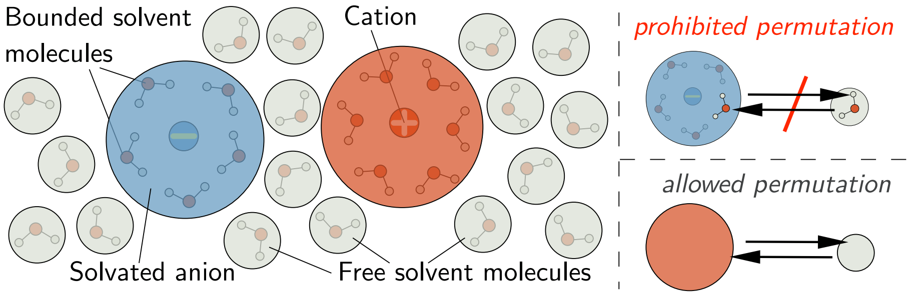

Figure 1: Each ion is supposed to bind some solvent molecules and forms a solvated ion. The mixture thus consists of free solvent molecules (gray), solvated anions (blue) and solvated cations (red). An exchange between a free and bounded solvent molecule is a prohibited permutation, while the exchanging a solvated ion and a free solvent is allowed.

leading to the number of possible configurations

$$W = \binom{\tilde{\mathcal{N}}}{\mathcal{N}_0^F, \mathcal{N}_1, \dots, \mathcal{N}_N} \tag{7}$$

and thus to a mixing entropy $S = k_{\text{B}} \ln(W)$ of

$$S = -k_{\text{B}} \left(\mathcal{N}_0^F \ln\left(\frac{\mathcal{N}_0^F}{\tilde{\mathcal{N}}}\right) + \sum_{\alpha=1}^{N} \mathcal{N}_\alpha \ln\left(\frac{\mathcal{N}_\alpha}{\tilde{\mathcal{N}}}\right)\right), \tag{8}$$

where the Sterling approximation has been used. Transition to particle number densities $\frac{\mathcal{N}_\alpha}{V} \to n_\alpha, \quad \alpha = 0, 1, \dots, N$ with $\tilde{n} = n_0^F + \sum_{\alpha=1}^{N} n_\alpha$ and the introduction of

$$\tilde{y}_0 := \frac{n_0^F}{\tilde{n}} \quad \text{and} \quad \tilde{y}_\alpha := \frac{n_\alpha}{\tilde{n}} \quad (\sum_{\alpha=0}^{N} \tilde{y}_\alpha = 1), \tag{9}$$

leads to a configurational entropy contribution of the free energy as

$$\rho\psi^S = k_{\text{B}} T \ \tilde{n} \left(\sum_{\alpha=0}^{N} \tilde{y}_\alpha \ln(\tilde{y}_\alpha) \right). \tag{10}$$

3 Mechanical contributions

Mechanical contributions to the free energy are derived from a simple linear elastic relation

$$p = p^R + K\left(\frac{V_{p^R}}{V} - 1\right) \tag{11}$$

where V_{p^R} is the volume of the mixture under pressure p^R. For the volume V_{p^R} a linear relation to the number of particles $\mathcal{N}_\alpha, \alpha = 0, 1, \dots, N$ is assumed, *i.e.*

$$V_{p^R} = \sum_{\alpha=0}^{N} v_\alpha^R(T, p^R)\, \mathcal{N}_\alpha, \tag{12}$$

where $v_\alpha^R(T,p^R)$ denotes the partial molar volume of species α at temperature T and reference pressure p^R. Note that $\mathcal{N}_0$ denotes here the total amount of solvent molecules. Using the relation between free solvent molecules $\mathcal{N}_0^F$ and bounded solvent molecules $\mathcal{N}_0^B$ gives

$$V_{p^R} = v_0^R\, \mathcal{N}_0^F + \textstyle\sum_{\alpha=1}^N (\kappa_\alpha\, v_0^R + v_\alpha^R)\, \mathcal{N}_\alpha. \tag{13}$$

Expectably, the partial molar volume a solvated ions consists of the volume of the central ion itself and the volume of κ_α solvent molecules ($\kappa_\alpha\, v_0^R + v_\alpha^R$). With

$$H := v_0^R\, \tilde{y}_0 + \textstyle\sum_{\alpha=1}^N (\kappa_\alpha v_0^R + v_\alpha^R)\, \tilde{y}_\alpha, \tag{14}$$

the pressure of the mixture is

$$p = p^R + K\,(\tilde{n}\, H(\tilde{y}_0, \tilde{y}_1, \ldots, \tilde{y}_{N-1}) - 1) \tag{15}$$

and hence dependent on the (local) composition. Since $p = -\frac{\partial \psi}{\partial \rho^{-1}}$ [6], where ρ denotes the mass density $\rho = \sum_{\alpha=0}^N m_\alpha n_\alpha$, one obtains the mechanical free energy

$$\rho\psi^M = (K - p^R)(1 - \tilde{n}\, H) + K\, \tilde{n}\, H \ln(\tilde{n}\, H) \tag{16}$$

upon integration and $\rho\psi^M$ vanishes for $p = p^R$.

4 Free energy and chemical potentials

The free energy of an electrolytic mixture is

$$\rho\psi = \sum_{\alpha=0}^N n_\alpha \psi_\alpha^R + \rho\psi^S + \rho\psi^M \tag{17}$$

where ψ_α^R denotes the free energy of species α in the reference state [1].

For $(T, n_0, \ldots, n_N)$ as independent variables, the chemical potentials of the (unsolvated) ions and (all) solvent molecules are defined as

$$\mu_\alpha(T, n_0, \ldots, n_N) = \frac{\partial\, \rho\psi}{\partial\, n_\alpha} \qquad \alpha = 0, 1, \ldots, N. \tag{18}$$

Note that the solvation effects are implicitly covered in the free energy function $\rho\psi$, independent of the set of variables. For the incompressible limit ($K \to \infty$) the new set of variables is $(T, p, \tilde{y}_1, \ldots, \tilde{y}_N)$[7] and the chemical potentials are

$$\mu_0 = \psi_0^R + k_{\mathrm{B}} T \ln(\tilde{y}_0) + v_0^R\, p \tag{19}$$

$$\mu_\alpha = \psi_\alpha^R + k_{\mathrm{B}} T \ln(\tilde{y}_\alpha) - k_{\mathrm{B}} T\ \kappa_\alpha \ln(\tilde{y}_0) + v_\alpha^R\, p. \tag{20}$$

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[1] There is a further contribution, *viz.* $-\frac{1}{2}\varepsilon_0\chi|\nabla\varphi|^2$, which, however, drops in the chemical potential for $\chi =$ const.

Note, incompressibility $K \to \infty$ implies $\frac{V_{pR}}{V} \to 1$ and thus

$$\tilde{n}\,(v_0^R\,\tilde{y}_0 + \textstyle\sum_{\alpha=1}^{N}(\kappa_\alpha v_0^R + v_\alpha^R)\,\tilde{y}_\alpha) \overset{!}{=} 1. \tag{21}$$

The free charge density q is related to the species densities via

$$q = e_0 \tilde{n} \textstyle\sum_{\alpha=1}^{N} z_\alpha \tilde{y}_\alpha. \tag{22}$$

5 Equilibrium properties

In equilibrium the following equations hold[5, 12, 7]

$$\nabla(\mu_\alpha - \tfrac{m_\alpha}{m_0}\mu_0) + e_0 z_\alpha \nabla\varphi = 0 \qquad \alpha = 1, \ldots, N \tag{23}$$

$$\nabla p = -q\nabla\varphi \tag{24}$$

$$\text{div}\;(\varepsilon_0(1+\chi)\nabla\varphi) = -q \tag{25}$$

$$\tilde{n}\,\big(v_0^R\,\tilde{y}_0 + \textstyle\sum_{\alpha=1}^{N}(\kappa_\alpha v_0^R + v_\alpha^R)\,\tilde{y}_\alpha\big) = 1 \tag{26}$$

which are the mass balances (23), the momentum balance (24), Poisson's equation (25) and the incompressibility constraint (26). The constraint (26) is simply used to compute $\tilde{n}$ and thus leading to

$$q = e_0 \frac{\sum_{\alpha=1}^{N} z_\alpha \tilde{y}_\alpha}{(v_0^R\,\tilde{y}_0 + \sum_{\alpha=1}^{N}(\kappa_\alpha v_0^R + v_\alpha^R)\,\tilde{y}_\alpha)}. \tag{27}$$

Next, note that from the momentum balance (24) and the mass balances (23) one concludes $\nabla\mu_0 = 0$[7]. With that, the linear combinations (for $\alpha = 1, \ldots, N$)

$$\nabla(\mu_\alpha + \kappa_\alpha \mu_0) = -e_0 z_\alpha \nabla\varphi \tag{28}$$

lead to the representation ($\alpha = 0, 1, \ldots, N$)

$$\tilde{y}_\alpha(\mathbf{x}) = \tilde{y}_\alpha^B\, \mathrm{e}^{-\frac{z_\alpha e_0}{k_\mathrm{B} T}(\varphi(\mathbf{x}) - \varphi^B) - \frac{(v_\alpha^R + \kappa_\alpha v_0^R)}{k_\mathrm{B} T}(p(\mathbf{x}) - p^B)}\,, \tag{29}$$

where the superscript ^{B} denotes the respective bulk values at $x = x_B$. Hence, all $\tilde{y}_\alpha$ are expressed as functions of φ and p and thus, according to eq. (27), $q = q(\varphi, p)$.

It is quite noteworthy that for an ideal, incompressible mixture (denoted by $^{\mathsf{IM}}$), which is obtained by setting $\kappa_\alpha = 0$ and $v_\alpha^R = v_0^R$, the pressure dependence in (27), with the representation (29), could be reduced and thus leading to $q = q^{\mathsf{IM}}(\varphi)$. Even though the pressure is reduced, it is **not** constant through the electrolyte[7]. In contrast, the classical *assumption* that the pressure p remains constant in the electrolyte, *i.e.* $p(\mathbf{x}) \equiv p^B$ (in addition to $\kappa_\alpha = 0$), leads to the Poisson–Boltzmann approximation (superscript $^{\mathsf{PB}}$) with $q = q^{\mathsf{PB}}(\varphi)$ ($q^{\mathsf{PB}} \neq q^{\mathsf{IM}}$).

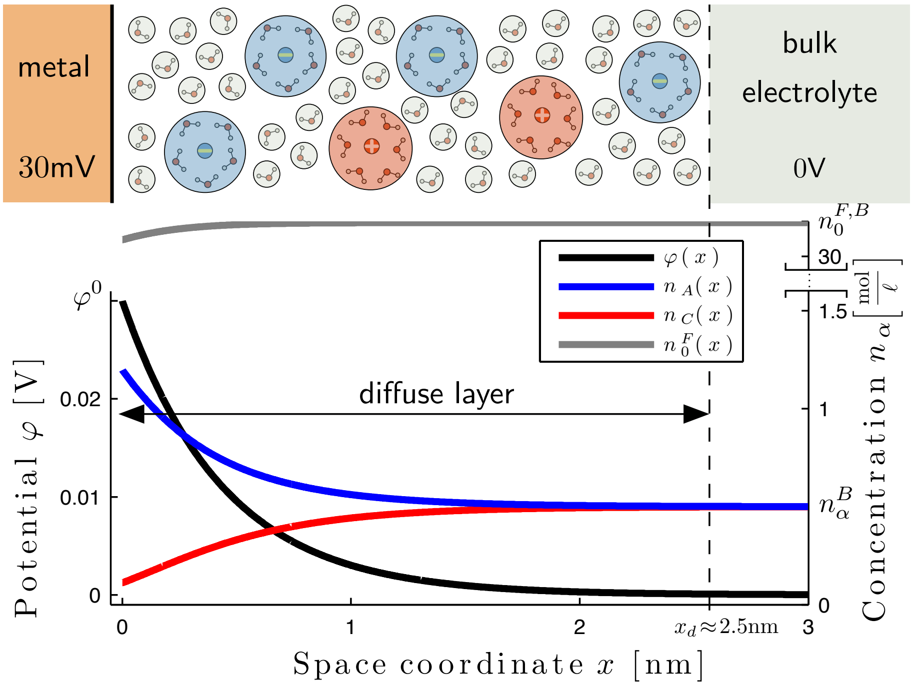

Figure 2: Numerical solutions of eqs. (24) & (25) for $\varphi^0 = 30$mV, representing the space charge layer within an electrolytic solution in contact with some inert metal. The *diffuse layer* is about 2.5nm wide and characterized by the deviations of the anion and cation concentrations $n_\alpha(x)$ from their respective bulk values n_α^B , $\alpha = \{A, C\}$.

6 The space charge layer in electrolytic solutions

The proposed model is now used to study the space charge layer of electrolytic solutions, *i.e.* the region where $q \neq 0$, for an externally applied potential $\varphi|_{x=0} = \varphi^0$. Exemplarily we consider a 0.5M KCl aqueous solution in contact with an *inert* metal, which means here that no adsorption onto the metal surface takes place. The mixture consist hence of constituents $\alpha = \{0, A, C\}$ with $z_A = -1$ and $z_C = 1$. Each ion is considered to bound $\kappa_\alpha = 15$ solvent molecules in its solvation shell and the specific volume v_α^R of constituents $\alpha = \{A, C\}$ is assumed to be equal to v_0^R. Equations (24)&(25), with (27)&(29), were solved in $1-D$ for the following boundary conditions and parameters:

$$\begin{array}{lll} \varphi|_{x=0} = \varphi^0 & \varphi|_{x=x_B} = 0 & \chi = 80 \\ p|_{x=0} = 1\text{atm} & v_0^R = 1.797\,10^{-3}\,\frac{\ell}{\text{mol}} & n_0^B = \frac{1}{v_0^R} \approx 55\,\frac{\text{mol}}{\ell} \\ \kappa_A = \kappa_C = 15 & n_A^B = n_C^B = 0.5\frac{\text{mol}}{\ell} & T = 293.75\text{K}. \end{array}$$

In the low potential regime ($\varphi^0 = 30$mV, FIG.2) the space charge layer is about $x_d = 2.5$nm wide (note that the Debye length for a 0.5M KCl aqueous solution is only $\lambda_D = 0.43$nm) and mainly characterized by an exponential-increase of $n_A(x)$ (blue line) and -decrease of $n_C(x)$ (red line) as function of the distance of the metal surface. Historically this layer is called *diffuse layer*, as the equilibrium concentration profiles $n_\alpha(x)$ result from the interplay of simple diffusion and electro-migration. However, since more anions are attracted from the metal surface, cations are pushed out of the charge layer, resulting in a net charge

$$Q := \int_0^{x_B} q(x)dx \qquad [\mu\text{C}\,\text{cm}^{-2}] \tag{30}$$

of about $Q(30\text{mV}) = -4.85\,\mu\text{C}\,\text{cm}^{-2}$. The potential distribution $\varphi(x)$ (black line) in the electrolyte shows also the well know exponential decay[2].

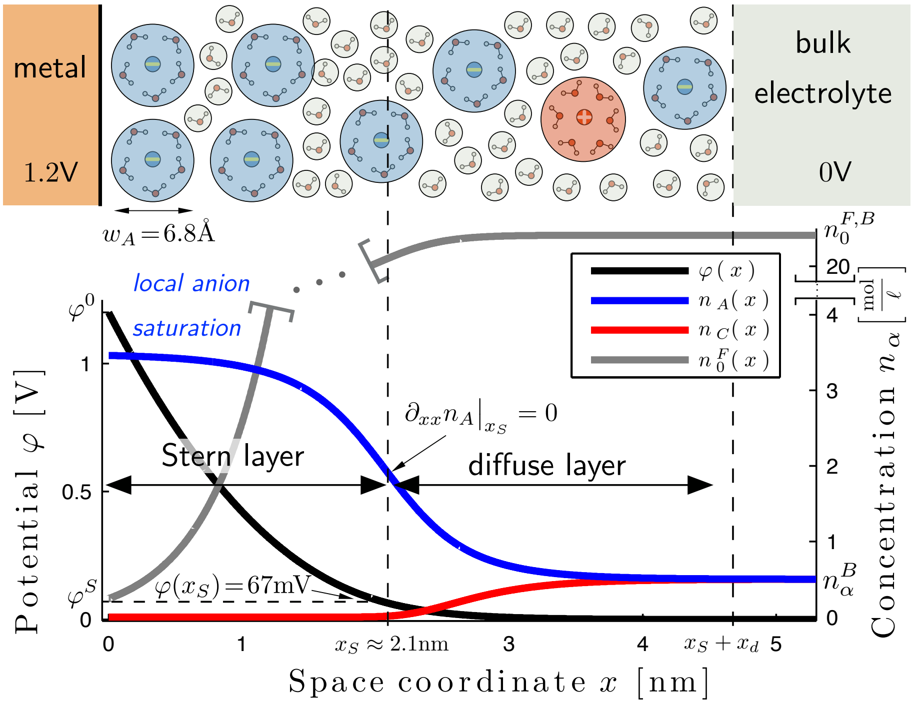

Figure 3: Space charge region at $\varphi^0 = 1.2$V with a characteristic Stern layer x_S of about 3 layers of solvated ions (≈ 21 Å). Due to the incompressibility constraint (26) a local increase of solvated anions entails a decrease of free solvent molecules and thus leads to a (local) saturation of anions.

At about $\varphi^0 = 75$mV the cation concentration at the metal surface starts to *vanish* and at $\varphi^0 = 280$mV the cation concentration is almost zero in the first nm in front of the metal surface. Increasing φ^0 further clearly entails an increasing anion concentration in the charge layer, and thus a decreasing net charge Q (*c.f.* FIG. 4). In order to fulfill the incompressibility constraint (26), the concentration of free solvent molecules has to decrease, which finally vanishes at about $\varphi^0 = 0.9$V closest to the metal surface. We call this anion saturation point, as only solvated anions are then present in front of the metal. Note that still solvent molecules are present in this layer, covered in the solvation shell (*c.f.* FIG. 3).

The specific width of a (ball shaped) solvated anion computes as $w_A = \sqrt[3]{6(v_A^R + \kappa_A\, v_0^R)\pi^{-1}} \approx 6.8$Å and one could ask for the potential at which the first layer of width w_A is *filled* with solvated anions. This layer is historically called Stern layer and describes the *specifically adsorbed solvated anions*. In our picture, however, the Stern layer is simply a **result** of the anion saturation, since solvation effects are covered in our free energy model (17). It is clear that the actual width of the Stern layer is highly dependent on the applied potential φ^0, and we suggest the *inflection point* of the anion concentration $n_A(x)$ as definition of the Stern layer width x_S (*i.e.* $\partial_{xx} n_A(x)\big|_{x_S} = 0, \partial_{xxx} n_A(x)\big|_{x_S} \neq 0$). The inflection point x_S was numerically computed for an external potential $\varphi^0 = 1.2$V as $x_S \approx 2.1$nm, which coincides with almost 3 layers of solvated ions in front of the metal.

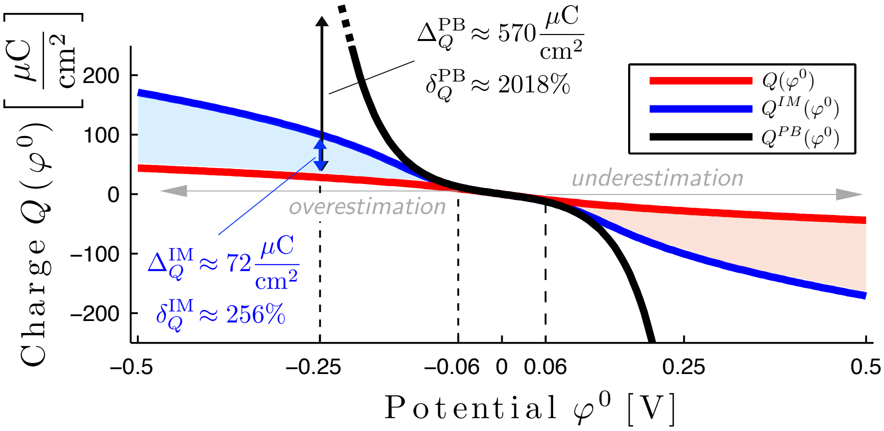

Figure 4: Charge Q stored in the double layer as function of the applied potential φ^0 for the PB approximation, the ideal mixture and our solvation model. Experimental data of the charge Q is in the order of $\pm(0-50)\mu$C cm^{-2} [9, 10], which is highly overestimated by the PB- and the ideal mixture model.

Finally, a comparison of the double layer charge Q between the Poisson–Boltzmann approximation, an ideal, incompressible mixture and our new solvation model is provided in FIG. 4. Until ± 60mV the models are *similar*, since the main contribution of the charge Q is the diffuse layer (*c.f.* FIG. 2). Thereafter the deviation of the (mixture) models becomes enormous. It is well known that experimental data of the double layer charge is in the order of $\pm(0-50)\,\mu$C cm^{-2} [9, 10]. At 0.25V, however, the PB approximation gives already $Q^{\mathrm{PB}} \approx 600\,\mu$C cm^{-2}, while $Q^{\mathrm{IM}} \approx 100\,\mu$C cm^{-2} and our new model predicts $Q \approx 28\mu$C cm^{-2}. The total error at $\varphi^0 = 0.25$V between the PB approximation and our solvation model is already $\Delta_Q^{\mathrm{PB}} = 570\,\mu$C cm^{-2}, with a relative error of $\delta_Q^{\mathrm{PB}} \approx 2018\%$! The incompressible, ideal mixture [7] is far better, however, still overestimating the charge at 0.25V by $\Delta_Q^{IM} = 72\,\mu$C cm^{-2} or $\delta_Q \approx 256\,\%$.

Bockris mentions that the “Gouy–Chapman theory might best be described as a brilliant failure” [2, p. 882], but the same holds true for the Poisson–Boltzmann approximation beyond 60mV. The incompressible, ideal mixture is a better approximation, however, we suggest our new mixture model as starting point for a rigorous thermodynamic description of electrolytic solutions.

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