



Short communication

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 metals. 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 model are: (i) the potential and pressure dependence of the free charge density in equilibrium (ii) the calculation of entropic contributions due to solvated ions, and (iii) the natural prediction of a solvated anion saturation layer which we finally reinterpret as Stern layer.

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First theoretical investigations of the space charge layer in electrolytic solutions date back around 100 years to the work of L. Gouy [1], D. Chapman [2] and O. Stern [3], 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 [4] on the capacity of the double layer, which were in disagreement to the commonly accepted theory at that time, gave the hint to Bikerman [5] in 1942 that the Boltzmann distribution ($n_\alpha \propto e^{-z_\alpha \varphi(x)}$) 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), 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

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

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 [6] 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 1 nm. For an extensive survey of the various continuum modeling approaches we refer to the instructive review of Bazant et al. [7].

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 modern material model for liquid electrolytes should be able to self-consistently predict the structure of the double layer, *i.e.* the decomposition of the Stern-layer and the diffuse layer.

In this letter we derive a free energy function which embodies solvation effects of the dissociated ions, in addition to mechanical stress, and calculate the chemical potentials of all constituents in the incompressible limit. With this, we show that in the thermodynamic equilibrium Eq. (1) is only a special case of the generic coupled equation system

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

$$\nabla p = -q(\varphi, p)\nabla\varphi, \quad (3)$$

which self consistently computes φ and the elastic pressure p . The model is then used (*i.e.* solved numerically) to propose the actual structure of the space charge region and its *a posteriori* decomposition in diffuse and Stern layer regions.

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Consider a mixture of \mathcal{N}_0 solvent molecules and \mathcal{N}_α , $\alpha = 1, \dots, N$ 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

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

In contrast, we consider a mixture in which some of the solvent molecules are *bounded* to the ions, forming solvated cations and anions [8]. Hence, the \mathcal{N}_0 solvent molecules split into \mathcal{N}_0^F free solvent molecules and \mathcal{N}_0^B bounded solvent molecules,

$$\mathcal{N}_0 = \mathcal{N}_0^F + \mathcal{N}_0^B. \quad (5)$$

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

$$\tilde{\mathcal{N}} = \mathcal{N}_0^F + \sum_{\alpha=1}^N \mathcal{N}_\alpha, \quad (6)$$

leading to the number of possible configurations

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

and thus to a mixing entropy $S = k_B \ln(W)$ of

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

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

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

leads to a configurational entropy contribution of the free energy as

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

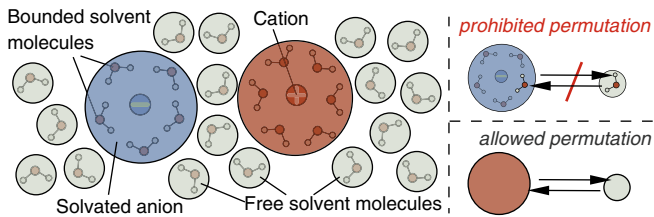


Fig. 1. Each ion is supposed to bind some solvent molecules and forms a solvated ion. The mixture thus consists of free solvent molecules (gray), solvated anions (blue) and solvated cations (red). An exchange between a free and bounded solvent molecule is a prohibited permutation, while exchanging a solvated ion and a free solvent is allowed. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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

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

where p is the elastic pressure, V_{p^R} the volume of the mixture under pressure p^R , and V the occupied volume [9]. For the volume V_{p^R} a linear relation to the number of particles \mathcal{N}_α , $\alpha = 0, 1, \dots, N$ is assumed, i.e.

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

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

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

Expectably, the partial molar volume of a solvated ion consists of the volume of the central ion itself and the volume of κ_α solvent molecules ($\kappa_\alpha v_0^R + v_\alpha^R := \tilde{v}_\alpha^R$, $\alpha = 1, \dots, N$). With

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

the pressure of the mixture is

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

and hence dependent on the (local) composition. Since $p = -\frac{\partial \psi}{\partial \rho}$ [10], where ρ denotes the mass density $\rho = \sum_{\alpha=0}^N m_\alpha n_\alpha$, one obtains the mechanical free energy

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

upon integration and $\rho \psi^M$ vanishes for $p = p^R$. The free energy density of an electrolytic mixture is thus

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

where ψ_α^R denotes the free energy of species α in the reference state (there is a further contribution, viz. $-\frac{1}{2} \epsilon_0 \chi |\nabla \phi|^2$, which, however, drops in the chemical potential for $\chi = \text{const}$).

For (T, n_0, \dots, n_N) as independent variables, the chemical potentials of the (unsolvated) ions and (all) solvent molecules are defined as [11]

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

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 ($K \rightarrow \infty$) the new set of variables is $(T, p, \tilde{y}_1, \dots, \tilde{y}_N)$ [9] and the chemical potentials are

$$\mu_0 = \psi_0^R + k_B T \ln(\tilde{y}_0) + v_0^R p \quad (19)$$

$$\mu_a = \psi_a^R + k_B T \ln(\tilde{y}_a) - k_B T \kappa_a \ln(\tilde{y}_0) + v_a^R p. \quad (20)$$

Note, incompressibility $K \rightarrow \infty$ implies $\frac{v_{p^R}}{V} \rightarrow 1$ and thus $\tilde{n} (v_0^R \tilde{y}_0 + \sum_{\alpha=1}^N (\kappa_\alpha v_0^R + v_\alpha^R) \tilde{y}_\alpha) = 1$.

The free charge density q is related to the species densities via $q = e_0 \tilde{n} \sum_{\alpha=1}^N z_\alpha \tilde{y}_\alpha$.

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