



Influence of the ion–solvent interactions on ionic transport through ion-exchange-membranes

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ABSTRACT

Ionic transport through ionic exchange membrane cannot be interpreted by the Nernst–Planck equation if the ion density is high, particularly in the membrane. In order to extend the density range, excess terms must be added to the chemical potential. These terms are computed by considering charged hard spheres embedded in a dielectric continuum. In this aim and owing to heterogeneity of the electrolytic solution the density function theory (DFT) is used. A previous work has been carried out with a homogeneous and amorphous solvent. Here an extension including the finite size of the solvent molecule and the local dielectric properties via the dielectric coefficient is presented. The electro-osmosis is also examined. The selectivity at equilibrium, the density profiles and the voltammograms are analysed. The numerical results obtained with NaCl and CaCl₂ show that the physical properties of the solvent decrease the selectivity and increases the conductivity of the membrane systems. In the same time, the dielectric properties increase the electro-osmotic effects on the ionic transport. The approach described in this work can be used to study the solvent confinement effect inside the membrane on the ionic transport.

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1. Introduction

The ion transfer and the spatial distribution of ionic species profiles in electrochemical systems are usually modelled by the Irreversible Thermodynamics (Onsager approach) or the Nernst–Planck (NP) equation [1–5]. Ion transfer is sometimes interpreted by the Stefan–Maxwell model [6]. In electrochemical engineering, the conductivity and the selectivity properties of these systems are described in a more realistic manner by taking into account of ion–ion and ion–solvent interactions by means of the Debye–Hückel activity coefficient, the Born solvation free energy and the electro-osmosis [4,7,8]. Another important mechanism rarely studied is the ion–membrane interaction via the ionic association [9].

Following the work of Gillespie et al. [10], the influence of the coulombic ion–ion interaction on the selectivity and the ion transport through an ion-exchange membrane has been studied in a previous paper [11] by coupling the Poisson–Nernst–Planck (PNP) equations with the Density Functional Theory (DFT). The DFT allows computing more rigorously the activity coefficient than the Debye–Hückel approach because it uses the direct correlation function calculated by the statistical thermodynamics of fluids [12,13]. Therefore this approach is more adapted to study the electrolyte structure at high density of ions and in confined

domain [14–16]. However the DFT applied to the ionic fluids uses the Mean Spherical Approximation (MSA) which assumes that the ions are charged hard spheres immersed in a homogeneous continuum dielectric [17]. This weakness is all the more important that the solvent molecule has a finite volume and that the dielectric coefficient is sensitive to the ion density.

In the present paper, we intend to use more realistic assumptions about the solvent properties. In this aim, the solvent is considered as a neutral hard sphere containing a dipole at its centre. Therefore two kinds of interaction are to be taken into account: the hard sphere and the ion–dipole one. In the present work, the ion–dipole interaction is not explicitly introduced in the variational approach of the DFT but is included in the dependence of the dielectric coefficient with respect to the ion density and in the MSA solvation free energy. Fawcett [18,19] and Vincze et al. [20] have shown that this method applied to homogeneous ionic fluids is able to compute the activity coefficient of simple electrolytes in water. In the present work, it is not introduced in the DFT in a rigorous way owing to the non-local character of the variational approach and owing to the unknown expression of the electrostatic excess term of the Helmholtz free energy functional. As a third kind of interaction, the finite volume of the ions and the solvation mechanism induce a solvent displacement called electro-osmosis.

Therefore, in a first part, the DFT–Poisson–Nernst–Planck (PNP/DFT) equation set are briefly introduced, the solvent hard sphere, the ion–dipole and the electro-osmosis are described. In a second

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part the numerical results are discussed. The effect of each interaction mentioned above on the selectivity at equilibrium, the density profiles and the transport properties are analysed separately. In Appendix A and B the DFT/MSA model is summarized and the numerical method is described respectively. The values of the numerical parameters are mentioned in Appendix B. The physical parameter values are gathered in Appendix C and in Table 1. Appendix D is devoted to the fulfilment of the electro-neutrality condition over the membrane system whatever the potential drop and the value of the water transport.

2. Membrane system and transport model

2.1. Description of the membrane system

The membrane system consists in a negatively charged membrane of length L embedded in a binary electrolyte solution the density of which is ρ_o . The two baths on both sides of the membrane have a length δ . So the membrane system length is $L+2\delta$. Along the membrane the fixed charge density Y is constant. We assume that the membrane and the ions do not interact chemically. The diffusion coefficient of species i D_i is constant over all the membrane system. Owing to the high values of ρ_o and of Y used in this work, the dependence of the dielectric coefficient ϵ with respect to the local ion concentration is taken into account. The salt is NaCl and CaCl₂. The solvent is water.

2.2. One-dimensional ion transport

Steady-state ion transport under concentration gradient and external field is defined by the divergence free of the flux of each species. If thermodynamic forces are small, the fluxes are linearly dependent on these forces and the following one-dimensional phenomenological relation is applied:

$$J_i = -\frac{D_i \rho_i(x)}{kT} \frac{\partial \mu_i}{\partial x} \quad (1)$$

where μ_i is the chemical potential defined at equilibrium, $\rho_i(x)$ the density of the species i located at x , k the Boltzmann constant, T the absolute temperature. The DFT is used to derive the expression of μ_i . The detail of the computation of μ_i in a bulk solution (without fixed charges) in which the dielectric coefficient is constant, is given in Refs. [10,21] and is briefly presented in Appendix A. With this approach, we obtain an extended Nernst–Planck (NP) equation to high concentration in which additional terms are associated to the ideal electrochemical potential μ_i^{ID} Eq. (A.2): and an electrostatic one μ_i^{ES} (Eq. (A.8)). The ions are charged hard sphere, i.e. the potential has an infinite value at a distance lower than R_i and has the coulombian expression at a distance higher than R_i . μ_i^{HS} represents the excluded volume effect of uncharged spherical particles and μ_i^{ES} , computed with the MSA, represents the ion size effect on the screening efficiency of the electrical double layer located around each ion. These two contributions depend on the density of all the ionic species. To the NP equation the Poisson equation must be added in order to compute the local electric potential Φ :

$$\frac{\partial}{\partial x} \left(\epsilon(x) \frac{\partial \Phi(x)}{\partial x} \right) = -e \sum_i z_i \rho_i(x) + Y(x) \quad (2)$$

where ϵ is the dielectric coefficient depending on the local electrolyte density and e is the elementary charge, z_i is the charge number of species i .

2.3. Contribution of the ion–dipole interaction

In the following, we will consider the solvent in a more realistic way. In the MSA, the solvent is only a homogeneous dielectric continuum characterized by its dielectric coefficient. Now the solvent is an uncharged hard sphere of radius R_w which contains at its centre an electrical dipole. The hard sphere and the electrical dipole contribution are treated separately. For the HS contribution, the solvent must be considered as a new species but uncharged and its transport obeys the NP equation. The dipole contribution is treated at two levels: in the ion–ion interaction via the dielectric coefficient ϵ and in the ion–dipole one via the solvation energy which depends on ϵ also.

If the ion density concentration is low, ion transport is usually computed assuming that the dielectric coefficient in the membrane and in the reservoir is the same. However ϵ depends on the local electric field strength. This effect is conventionally named dielectric saturation [26,27]. The high strength of the electric field is located inside the membrane and results from the fixed charges at the pore surface. It is also located at the bath/membrane or membrane/membrane interface in the over-limiting regime. Usually the dielectric saturation is taken into account when the influence of ion association or proton transport or water dissociation on the separation efficiency or on the conductivity is studied [28–31].

In the present work, this phenomena is not taken into account. The dielectric coefficient of the solute in the membrane and in the reservoir depends on the salt density in the same way. The concentration dependence of ϵ is considered as given (see Appendix C).

In homogeneous electrolytes, the MSA links the chemical potential to the first derivative of the Helmholtz free energy with respect to the density and the direct correlation function to the second derivative. These derivatives are carried out with Γ kept constant. In inhomogeneous electrolyte, the same relations are used but in the functional sense. However, in the variational approach, the ES Helmholtz free energy functional is unknown. This is why μ_i^{ES} is expanded with respect to the density around a reference fluid (Eq. (A.8)): the zeroth order term is the MSA chemical potential function and the expression of first order term, i.e. the direct correlation function, is deduced from the computation of the electrostatic free energy of two overlapping charged shells [22].

If we take into account of the dependence of ΔJ^{SOL} with respect to the electrolyte composition, the following derivative must be used:

$$\frac{\partial}{\partial \rho_i} = \frac{\partial}{\partial \rho_i} \Big|_{\Gamma = \rho_k(k \neq i) = \epsilon = cst} + \frac{\partial \epsilon}{\partial \rho_i} \frac{\partial}{\partial \epsilon} \Big|_{\Gamma = \rho_k(k \neq i) = cst} \quad (3)$$

where Γ is the MSA screen parameter. So the zeroth order term of the expansion is the corrected MSA chemical potential suggested by Fawcett [19] and Simonin et al. [23] but with the ionic radius kept constant. However, the derivatives must be carried out in the reference fluid (see Appendix A). Using Eqs. (A.8) and (3), the first order term becomes:

$$\begin{aligned} & kT \sum_j \int \left(\frac{\delta^2 A^{ES} [\{\rho_k^{ref}(y)\}]}{\delta \rho_i^{ref}(x) \delta \rho_j^{ref}(x')} \right) \Delta \rho_j(x') dx' \\ & + kT \sum_j \int \left(\frac{\partial \epsilon}{\partial \rho_i^{ref}(x)} \frac{\delta^2 A^{ES} [\{\rho_k^{ref}(y)\}]}{\delta \epsilon(x) \delta \rho_j^{ref}(x')} + \frac{\partial \epsilon}{\partial \rho_j^{ref}(x')} \frac{\delta^2 A^{ES} [\{\rho_k^{ref}(y)\}]}{\delta \epsilon(x') \delta \rho_i^{ref}(x)} \right) \\ & + \frac{\delta^2 A^{ES} [\{\rho_k^{ref}(y)\}]}{\delta \epsilon(x') \delta \epsilon(x)} \Delta \rho_j(x') dx' \end{aligned} \quad (4)$$

where $\epsilon(x) = \epsilon(\rho_k^{ref}(x))$, ρ_k^{ref} is the density of species i in the reference fluid (Eq. (A.9)) and A^{ES} is the free energy functional.

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