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Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Ion transport dependence on the ion pairing/solvation competition in cation-exchange membranes

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ARTICLE INFO

Article history:

Received 7 July 2014

Received in revised form

22 December 2014

Accepted 29 January 2015

Available online 11 February 2015

Keywords:

Ionic transport

Density functional theory

Activity coefficient

Ion association

Solvation

ABSTRACT

Effect of ion-pairing on ion partitioning at equilibrium and on transport properties is studied by means of the Poisson–Nernst–Planck (PNP) equations. Owing to the low electrolyte solution relative permittivity (ϵ_s) and the high ion density in the membrane, the excess terms of the chemical potential must be computed. In this aim, the density functional theory and the binding mean sphere approximation were used in order to extend the PNP equations and to compute the association constant. The counter-ion/ fixed-charge-group pairing and the counter-ion/co-ion one were examined. In the case of monovalent fixed charge, the total density of co-ion and the free one decreases with ϵ_s owing to the solvation contribution. So that it induces a decrease of the membrane system conductivity. If the counter-ion/co-ion pairing is considered, the free co-ion density and the conductivity increase when ϵ_s reaches small values. However in the ohmic regime, this dependence of the conductivity towards the free co-ion density is not always fulfilled.

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1. Introduction

Several mechanisms such as dielectric exclusion, Born solvation, ion pairing or membrane heterogeneity may explain the failure of the Donnan equilibrium theory even at small salt concentration [1–6]. In particular the ion association between fixed charge groups and counter-ions induces a neutralization of the fixed charge sites and a decrease of the selectivity affecting the ion transport mechanism [4–8]. It seems that the presence of ion association between the counter-ions and fixed charge groups has been revealed by NMR investigations [9]. The ion pairing is an electrostatic phenomenon [10]. So its intensity is all the more important that the local relative permittivity is small. This can be encountered if the solution contains an organic solvent or if the membrane contains a small amount of water [4–7]. However the high electric field at the pore surface induced by the high surface charge leads to a dielectric saturation whatever the context [11–14].

Abbreviations: DCA, distance of closest approach; DFT, density functional theory; EDL, electric double layer; ES, electrostatic; HS, hard sphere; LCR, limiting current regime; MAL, mass action law; MSA, mean spherical approximation; OR, ohmic regime; PNP, Poisson–Nernst–Planck (equation set); SOL, solvation; h0,1,2, ion pairing models

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Studies on association phenomenon in membrane systems are usually carried out by means of the Donnan equilibrium theory and the Nernst–Planck (NP) transport equation coupled to the mass action law representing the association process. The equilibrium constant of pairing is modelled by the Fuoss formalism [4–7,15]. Experimental results and theoretical ones depend on the estimation of several parameters such as the relative permittivity, the ion size, the activity coefficient, the ion mobility in membranes. As in the two previous articles [16,17], the statistical thermodynamic approach is used in order to compute more rigorously the excess terms of the chemical potential in the presence of ion pairing. In this aim, the density functional theory (DFT), developed by Rosenfeld [18,19] and improved by Gillespie et al. [20,21], coupled with the binding mean sphere approximation (BIMSA-EXP) model developed at the PHENIX lab.[22–24] extends the NP equation to high microscopic ion–ion interactions such as the hard sphere and the electrostatic ones. Many theoretical investigations of association between neutral or ionic species have been carried out with the DFT approach in many situations such as charged surfaces, slits, liquid–vapor interfaces [25–31]. However these investigations were made at equilibrium. In the case of the ionic species, the agreement with the Monte-Carlo simulations has shown that taking into account of ion association improves the description of the 1–1 electrolyte structure along a charged surface [30]. However despite the thorough description of this approach, the center-to-center distance of the ion pair

remains an estimated parameter and the bulk is assumed to be a homogeneous dielectric continuum.

The goal of the paper is neither to prove the existence nor to give a new insight of the ion pairing mechanism in ion-exchange membrane but to propose a more rigorous way to compute the ion pairing thermodynamics. This model among others [10] seems, to my knowledge, to be ignored in the membrane separation engineering. So the numerical results will show also the weaknesses of the approach analyzed in this paper.

Two cases are examined in this investigation: the case in which the usual counter-ions/fixed charge groups association is taken into account and the case in which coexists a second association process occurring between the co-ions and the counter-ions. In these two association models the fixed species is monovalent. The divalent case is commented in the [Supplementary information section](#). The use of the DFT and of the BIMSA-EXP model in the context of ion separation in membrane systems needs to make some approximations. Contrary to the above investigations in which the association process occurs in the bulk, the association between the fixed charge group and the counter-ion occurs at the pore surface where the relative permittivity is certainly much lower than at the pore center [13,14]. Therefore in this study the fixed charge is considered as an additional ionic species without any distinction with the others but fixed and the relative permittivity is assumed to be a quantity averaged over the pore volume. Despite the variation of the relative permittivity at the bath/membrane interface, the expression of the thermodynamic quantities is assumed to be valid, i.e. each elementary volume of fluid is considered homogeneous.

In the next section, after introducing the DFT–Poisson–Nernst–Planck (DFT/PNP) equation set and the solvation model, the BIMSA-EXP model of association is described. The computation of the association parameters is summarized and the modification of the NP transport equation induced by the ion pairing is commented. In a second part the numerical results are examined. At equilibrium the ion partitioning is analyzed first for a wide range of solute relative permittivity inside the membrane. The comparison with the Fuoss model and the Bjerrum one and the sensitivity to the ion size are then analyzed. Finally the numerical results at equilibrium and their analysis are used in the interpretation of the current–voltage curves. The expression of the electrostatic contribution to the excess part of the chemical potential modified by the association is written in [Appendix A](#). In [Appendix B](#), the computation of the derivative of the free ion fraction with respect to the total density is summarized. This term is used in order to compute the MAL contribution of the chemical potential. The numerical method is described in [Appendix C](#). The physical parameter values are gathered in this Appendix and in [Table 1](#). In [Appendix D](#), the numerical simulations carried out at equilibrium are compared to experimental data.

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 $L + 2\delta$. As in the previous papers, L and δ are equal to 50 and 100 times the Debye length (Eq. (C.6) in [Appendix C](#)) respectively. Along the membrane the fixed charge density Y is constant. However at the vicinity of the bath/membrane interfaces the fixed charge density profile follows a hyperbolic tangent in order to avoid a discontinuity (Eq. (C.4) [Appendix C](#)). The depth of variation

Table 1

Molecular parameters used in the computations: ionic radius, solvation radius and solvation free energy density.

Ion	R_i (Å)	R_i^{sol} (Å) ^a	$\mu_i^{sol}(\epsilon_S = \epsilon_W)$ (kJ/mol) ^a
Na ⁺	1	1.62	−424
Cl [−]	1.8	2.26	−304

^a The solvation radius R_i^{sol} and the solvation free energy density μ_i^{sol} were found in Vincze et al. [44].

of Y (σ_X) is much smaller than L . The diffusion coefficient of species i (D_i) is identical whatever the species and is constant over all the membrane system but the relative permittivity of the electrolyte solution (ϵ_S) inside the membrane is lower than in the reservoirs. At the vicinity of the bath/membrane interfaces, ϵ_S follows the same profile as the fixed charge density (Eq. (C.4) [Appendix C](#)). The salt is NaCl and the solvent is water. Contrary to previous works [16,17], we assume that the membrane and the ions interact through the ion pairing. In the following the fixed charge will be assimilated to a third ionic species but fixed: $Y = z_3 \rho_3$ (species 1 and 2 being Na⁺ and Cl[−] respectively). The charge number z_3 is equal to -1 . In this work we assume also that ϵ_S does not depend on the local density.

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 flux is linearly dependent on these forces and the following one-dimensional phenomenological relation is applied:

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

where μ_i is the chemical potential per particle defined at equilibrium, $\rho_i(x)$ the particle density of the species i located at x , k the Boltzmann constant, and T the absolute temperature. The DFT is used in order to derive the expression of μ_i . It describes the thermodynamic equilibrium of inhomogeneous systems submitted to an external force, in contact with a reservoir characterized by a temperature T and a chemical potential μ [32–34]. At equilibrium, the temperature and the chemical potential of these systems must be equal to those of the reservoir. In the case of ionic fluids, the electrolyte is assumed to be a mixture of species i which are hard spheres of radius R_i and of charge number z_i , 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 . The species are immersed in a solvent which is a dielectric continuum. The equilibrium distribution of density is calculated by minimization of the grand canonical potential with respect to the species density $\rho_i(x)$. The minimization leads to

$$\mu_i = \frac{\delta A \left[\left\{ \rho_j(x') \right\} \right]}{\delta \rho_i(x)} = \mu_i^{ID}(x) + \mu_i^{HS}(x) + \mu_i^{ES}(x) \quad (2)$$

where A is the Helmholtz free energy expressed as a functional of the local density $\{\rho_j(x')\}$, $\delta/\delta\rho_i(x)$ means the functional derivative. With this approach, we obtain an extended NP equation in which additional terms are associated with the ideal electrochemical potential μ_i^{ID} : a hard sphere contribution μ_i^{HS} and an electrostatic one μ_i^{ES} . μ_i^{HS} represents the excluded volume effect in a fluid constituted of uncharged spherical particles and μ_i^{ES} represents the ion size effect on the screening efficiency of the electrical double layer located around each ion. μ_i^{ES} can be computed with the Debye–Hückel approach but in this work we use the MSA model

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