



# Accounting for frame of reference and thermodynamic non-idealities when calculating salt diffusion coefficients in ion exchange membranes



Jovan Kamcev<sup>a</sup>, Donald R. Paul<sup>a</sup>, Gerald S. Manning<sup>b</sup>, Benny D. Freeman<sup>a,\*</sup>

<sup>a</sup> McKetta Department of Chemical Engineering, Center for Energy and Environmental Resources, and Texas Materials Institute, The University of Texas at Austin, 10100 Burnet Road Building 133 (CEER), Austin, TX 78758 USA

<sup>b</sup> Department of Chemistry and Chemical Biology, Rutgers University, 610 Taylor Road, Piscataway, NJ 08854-8087, USA

## ARTICLE INFO

### Keywords:

Ion exchange membrane  
Salt diffusion  
Salt sorption  
Frame of reference  
Non-ideal

## ABSTRACT

Accurate evaluation of salt diffusion coefficients from transport rate data in ion exchange membranes requires accounting for frame of reference and non-ideal thermodynamic effects. Due to a lack of models and experimental data quantifying membrane ion activity coefficients, it has been impossible to evaluate the impact of non-ideal thermodynamic effects on observed salt diffusion coefficients. Here, a framework is presented that includes both frame of reference (i.e., convection) and non-ideal thermodynamic effects in calculating salt diffusion coefficients in ion exchange membranes. Effective concentration averaged NaCl diffusion coefficients were determined as a function of upstream NaCl concentration in commercial ion exchange membranes from NaCl permeability and sorption measurements via the solution-diffusion model. Frame of reference effects were evaluated using a version of Fick's law that accounts for convection. The factors necessary to account for non-ideal thermodynamic effects were developed using Manning's counter-ion condensation theory. At low upstream NaCl concentrations, frame of reference and non-ideal thermodynamic effects on diffusion coefficients were negligible. However, at higher upstream NaCl concentrations (e.g., > 0.1 M), both effects contribute measurably to NaCl diffusion coefficients. Correcting for frame of reference effects increased apparent NaCl diffusion coefficients. However, correcting for thermodynamic non-idealities of the ions sorbed into the membranes reduced apparent NaCl diffusion coefficients. Fortunately, for the materials considered in this study, frame of reference and non-ideal thermodynamic effects nearly cancel each other.

## 1. Introduction

Ion exchange membranes (IEMs) (i.e., charged membranes, ionomers, etc.) are necessary for several membrane-based technologies (e.g., electrodialysis, reverse electrodialysis, fuel cells, etc.), and they are actively being explored for use in other applications (e.g., reverse osmosis, forward osmosis, etc.) [1–14]. IEMs are made from polymers having ionizable functional groups covalently bound to their backbone [15]. Sorption of polar solvents (e.g., water) into such polymers can lead to dissociation of the fixed charge groups and membrane swelling, which facilitates water and ion transport through such materials [15]. The charged character of IEMs has a profound impact on both ion sorption and transport [6,15–20]. However, a complete molecular understanding of the fixed charged group influence on ion sorption and diffusion in such materials is still evolving [6]. Fundamental structure/property studies are needed for rational design of high performance membranes with specifically tailored transport properties [6,18]. Developing such relationships hinges on the ability to interpret

experimental findings within a robust, fundamentally based modeling framework.

Experiments in which a membrane separates two aqueous salt solutions of different concentrations are often used to probe salt transport in membranes and determine transport parameters (e.g., salt diffusion and permeability coefficients) [15,17,21,22]. In such experiments, the electrochemical potential difference between the two solutions is the driving force for ion transport through the membrane [15,21,23]. In the absence of an externally applied electric field, the electrochemical potential gradient reduces to a thermodynamic activity gradient [15,21,23]. In practice, it is more convenient to measure salt concentrations, rather than salt activities, in aqueous solutions or membranes. Consequently, the driving force for salt transport is often expressed in terms of a salt concentration gradient. However, transport properties computed using a driving force based on concentration gradients rather than activity gradients result in salt diffusion coefficients that implicitly contain a thermodynamic factor, which could complicate a fundamental interpretation of such properties [24].

\* Corresponding author.

E-mail address: [freeman@che.utexas.edu](mailto:freeman@che.utexas.edu) (B.D. Freeman).

## Nomenclature

$A_m$	geometric area available for mass transfer in salt permeability measurements
$(C_s^s)_0$	upstream solution mobile salt concentration
$(C_s^s)_L$	downstream solution mobile salt concentration
$(C_s^m)_0$	membrane mobile salt concentration at the upstream face
$\langle \bar{D}_s^{m*} \rangle$	apparent salt diffusion coefficient (includes contribution from both convection and thermodynamic non-idealities)
$\langle D_s^{m*} \rangle$	effective average salt diffusion coefficient (includes thermodynamic non-idealities)
$D_s^{m*}$	effective local salt diffusion coefficient (includes thermodynamic non-idealities)
$D_s^m$	local salt diffusion coefficient
$D_i^m$	diffusion coefficient of ion $i$ in membrane ( $i = c$ for co-ions and $i = g$ for counter-ions)
$D_i^s$	diffusion coefficient of ion $i$ in solution ( $i = c$ for co-ions and $i = g$ for counter-ions)
$d_w$	density of water
$\gamma_g$	counter-ion activity coefficient
$\gamma_c$	co-ion activity coefficient
$j_i$	diffusive mass flux of salt
$K_s$	salt sorption coefficient
$L$	hydrated membrane thickness

$M_s$	molecular mass of salt
$n_s$	combined mass flux of salt
$n_p$	combined mass flux of polymer
$n_w$	combined mass flux of water
$\nu_g$	number of counter-ions in one salt molecule
$\nu_c$	number of co-ions in one salt molecule
$\omega$	fixed charge group valence
$\omega_s$	mass fraction of salt
$(\omega_s)_0$	mass fraction of salt at the upstream face of a membrane
$\langle P_s \rangle$	average salt permeability coefficient
$P_w$	hydraulic water permeability coefficient
$\Delta p$	hydrostatic pressure difference across a membrane
$\Delta \pi$	osmotic pressure difference across a membrane
$\pi_0$	upstream solution osmotic pressure
$\pi_L$	downstream solution osmotic pressure
$\rho_s^m$	mass concentration of salt in a membrane
$(\rho_s^m)_0$	mass concentration of salt in a membrane at the upstream face
$(\rho_s^m)_L$	mass concentration of salt in a membrane at the downstream face
$V$	volume of upstream and downstream solutions in salt permeability measurements
$x$	direction of mass transfer (along the membrane thickness)

Salt diffusion coefficients calculated based on a concentration gradient driving force are “effective” values containing both thermodynamic and kinetic contributions, with the thermodynamic contribution coming from the effect of ion concentration on ion activity coefficients [25]. The kinetic component of the effective salt diffusion coefficient measures salt mobility due to random Brownian motion. In principle, the kinetic component of effective salt diffusion coefficients, which can be obtained by properly accounting for thermodynamic non-idealities, should be comparable to diffusion coefficients obtained from radioactive tracer techniques. In experiments using radioactive tracers, the system is typically at equilibrium. Thus, no gradients in activity, and therefore activity coefficients, exist, if the radioactively labeled species are chemically identical to those that are not [15,26,27].

In the simplest experimental configuration, a flat membrane separates two aqueous salt solutions having different concentrations of salt, as shown in Fig. 1. The hydrostatic pressure is the same on both sides of the membrane. Salt transport occurs from the high to low concentration side of the membrane or film. Consequently, there is also a difference in water concentration in the two solutions, which drives water transport in the opposite direction to salt transport due to osmosis. Water transport by osmosis can influence experimentally measured salt diffusion coefficients, since such measurements are typically analyzed relative to a stationary frame of reference (i.e., the laboratory) [18,28]. The flux appearing in Fick's first law in its most familiar form (i.e.,  $j = -DVC$ ) is the diffusive flux and does not account for convective (i.e., frame of reference) effects [29]. This equation must be modified to account for frame of reference effects to obtain salt diffusion coefficients that do not inherently include a convection contribution. These effects are known to significantly influence water (and other liquid) diffusion in highly swollen membranes [18,28,30,31]. However, to the best of our knowledge, studies probing frame of reference effects on salt diffusion in dense membranes and, in particular, charged membranes, are currently not available.

Structure/property relations for salt transport in membranes can be better understood by quantifying frame of reference and non-ideal thermodynamic effects for evaluation of diffusion coefficients, since such effects could be significant in some cases, resulting in behavior in observed (or effective) salt diffusion coefficients that could be erroneously attributed to membrane characteristics. For example, instances

where non-ideal thermodynamic effects on diffusivity of gases in polymers are substantial have been reported [24]. The influence of frame of reference effects on solvent and water transport in highly swollen polymer membranes has also been reported [30,31].

In this study, we explore concentration gradient driven NaCl transport through negatively charged (i.e., cation exchange membranes, CEMs) and positively charged (i.e., anion exchange membranes, AEMs) membranes. A new framework to evaluate frame of reference and non-ideal thermodynamic effects on salt diffusion coefficients is presented. Frame of reference effects were quantified using a rigorous version of Fick's law. Single ion activity coefficient data as a function of ion concentration in IEMs is needed to quantify non-ideal thermodynamic effects. However, these values cannot be determined experimentally, so a theoretical model for ion activity coefficients in charged polymers is needed. We recently proposed a new, experimentally verified model of ion activity coefficients in IEMs, based on Manning's counter-ion condensation theory [16,19]. Manning's model provides a convenient tool for estimating the necessary thermodynamic factors, allowing one to readily decouple the kinetic and thermodynamic components of effective salt diffusivity in a membrane. To the best of our knowledge, this study represents the first time non-ideal

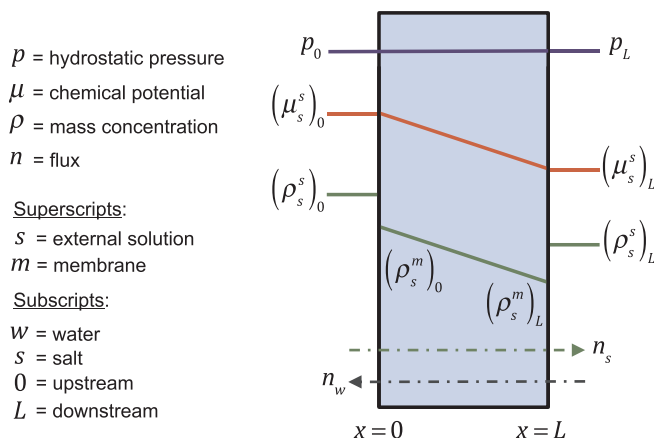


Fig. 1. Schematic of a dense (i.e., non-porous) polymeric membrane surrounded by aqueous salt solutions having different concentrations.

Download English Version:

<https://daneshyari.com/en/article/4988849>

Download Persian Version:

<https://daneshyari.com/article/4988849>

[Daneshyari.com](https://daneshyari.com)