Eur. Phys. J. Special Topics **227**, 2515–2538 (2019)

https://doi.org/10.1140/epjst/e2019-800133-2

THE EUROPEAN
PHYSICAL JOURNAL
SPECIAL TOPICS

Regular Article

The impact of solvation and dissociation on the transport parameters of liquid electrolytes: continuum modeling and numerical study

Wolfgang Dreyer, Clemens Guhlke[a], and Rüdiger Müller

Weierstrass Institute, Mohrenstr. 39, 10117 Berlin, Germany

Received 23 August 2018 / Received in final form 28 September 2018

Abstract. Electro-thermodynamics provides a consistent framework to derive continuum models for electrochemical systems. For the application to a specific experimental system, the general model must be equipped with two additional ingredients: a free energy model to calculate the chemical potentials and a kinetic model for the kinetic coefficients. Suitable free energy models for liquid electrolytes incorporating ion–solvent interaction, finite ion sizes and solvation already exist and have been validated against experimental measurements. In this work, we focus on the modeling of the mobility coefficients based on Maxwell–Stefan setting and incorporate them into the general electro-thermodynamic framework. Moreover, we discuss the impact of model parameter on conductivity, transference numbers and salt diffusion coefficient. In particular, the focus is set on the solvation of ions and incomplete dissociation of a non-dilute electrolyte.

1 Introduction

Continuum models are an indispensable tool to study electrochemical phenomena on the device level. Recently, a general modeling framework was derived in the context of electro-thermodynamics for electrochemical systems [9,12]. The ingredients of the models are chemical potentials, derived from a free energy density, and kinetic parameters like mobilities for ion diffusion. A suitable free energy model for liquid electrolytes, which is capable to handle solvent–ion interaction, finite ion size and solvation, is developed in [6,9]. The model is validated against experimental measurements of differential capacitance of single crystal surfaces and electrocapillarity curves for aqueous electrolytes [7,15]. The main scope of this paper is the modeling of the kinetic parameters, i.e. the mobility coefficients, and an evaluation of the resulting transport properties of the electrolyte. In particular, we study the dependence of the transport parameters on ion solvation and dissociation reaction.

We apply Maxwell–Stefan setting for multicomponent transport diffusion laws for the derivation of the mobility coefficients, cf. [1,24,25,27]. However, instead of the

---

[a] e-mail: clemens.guhlke@wias-berlin.de

mobility coefficients, often other transport parameters are more useful for the interpretation of measurements. In the context of energy conversion systems, the electric conductivity of electrolytes has naturally attracted most interest. Further relevant parameters are the transference numbers and diffusion coefficients. In contrast to the equilibrium properties, some of these mentioned transport properties depend on a combination of chemical potentials and kinetic coefficients, while others depend solely on the kinetic coefficients.

In the literature, two distinct transport theories are commonly used, one for dilute solutions and one for concentrated solutions, see e.g. [18,20]. The dilute solution theory is based on Nernst–Planck theory, whereas in the concentrated solution case Maxwell–Stefan theory is applied. However, there was some controversy about discrepancies between these two theories, cf. [22]. As pointed out in [3] this discrepancy is only apparent and can be attributed to the use of different potentials in the two settings. In this paper, we present one general framework to cover concentrated and strongly diluted solutions in the same setting.

We perform a numerical assessment of the obtained continuum model. The applied electrolyte model for liquid electrolytes contains solvated ions, i.e. complexes build from a center ion and a solvation shell containing a certain number solvent molecules. We study the impact of the solvation on the transport parameters. In a non-dilute solution, the neutral salt in general will dissociate only partially into anions and cations. Therefore, we also investigate transport coefficients for electrolytic mixtures that contain the undissociated salt as an additional constituent.

Outline. We start by summarizing a general continuum model for electrolytes in Section 2. Section 3 contains the constitutive modeling of a liquid electrolyte. We summarize a bulk free energy model and derive a framework for the mobility coefficients. In Section 4, we discuss the dilute solution limit and electroneutral bulk transport. The numerical evaluation of the model is done in Section 5. We start with a numerical study for a binary electrolyte with a completely dissociated salt, where explicit expressions for the transport parameters can be derived. Next, we extend the model to study the transport parameters of an electrolyte with partially dissociated salt. The work closes with conclusions and outlook in Section 6.

2 Electro-thermodynamics

The following model is derived from a general continuum model for magnetizable, polarizable, elastic, viscous, heat conducting and reactive mixtures [12]. To simplify the model, we are only interested in electrostatic and isothermal processes. In consequence, the magnetic field can be ignored whereas the temperature T still appears in the equations, but only as a constant parameter. The applied notation is summarized in Table 1.

Constituents and chemical reactions. The electrolyte is modeled as a mixture of $N+1$ constituents A_α indexed by $\alpha \in \{0,1,2,\ldots,N\}$. Each of constituent A_α is characterized by the (atomic) mass m_α and its atomic charge $z_\alpha e_0$, where the positive constant e_0 is the elementary charge and z_α is the charge number of the constituent.

There may be $M \geq 0$ chemical reactions in the mixture, where the reactions may be written in the general form

$$\sum_{\alpha=0}^{N} a_\alpha^k \mathrm{A}_\alpha \underset{R_b^k}{\overset{R_f^k}{\rightleftharpoons}} \sum_{\alpha=0}^{N} b_\alpha^k \mathrm{A}_\alpha \qquad \text{for } k \in \{1,\ldots,M\}. \tag{1}$$

Table 1. Summary of notations.

k_B (J/K)	– Boltzmann constant	e_0 (C)	– Elementary charge
ε_0 (C/V m)	– Electric constant	χ	– Susceptibility
m_α (kg)	– Atomic masses	z_α	– Charge number
ν_α^k	– Stoichiometric coefficients		
φ (V)	– Electrostatic potential	T (K)	– Bulk temperature
ρ_α (kg/m^3)	– Partial mass density	ρ (kg/m^3)	– (Total) mass density
n_α (1/m^3)	– Number density	n (1/m^3)	– Total number density
$\boldsymbol{v}_\alpha$ (m/s)	– Partial velocity	$\boldsymbol{u}$ (m/s)	– Relative velocity
$\boldsymbol{v}$ (m/s)	– Barycentric velocity	$\rho\psi$ (J/m^3)	– Free energy density
μ_α (J)	– Chemical potential	μ_α^e (J)	– Electrochemical potential
$\boldsymbol{J}_\alpha$ (1/sm^2)	– Mass flux density	R^k (1/sm^3)	– Reaction rates
$\boldsymbol{\Sigma}$ (Nm)	– Total stress tensor	p (Nm)	– Pressure
$M_{\alpha\beta}$ (s/kg m^3)	– Mobility	$\mathcal{D}_{\alpha\beta}$ (m^2/s)	– Maxwell–Stefan diffusivities
$f_{\alpha\beta}$	– Friction coefficients	D (m^2/s)	– Salt diffusion coefficient
t_α	– Transference numbers	σ (S/m)	– Conductivity

The constants a_α^k, b_α^k are non-negative integers and $\nu_\alpha^k := b_\alpha^k - a_\alpha^k$ denote the stoichiometric coefficients of the reactions. The reaction from left to right is called forward reaction with reaction rate $R_f^k > 0$ and $R_b^k > 0$ is the reaction rate of the backward reaction. The net reaction rate R^k is defined as $R^k = R_f^k - R_b^k$.

Since both charge and mass are conserved in each single reaction, we have

$$\sum_{\alpha=0}^{N} z_\alpha \nu_\alpha^k = 0 \qquad \text{and} \qquad \sum_{\alpha=0}^{N} m_\alpha \nu_\alpha^k = 0 \qquad \text{for } k \in \{1,\ldots,M\}. \tag{2}$$

Thermodynamic state. In the isothermal electrostatic setting the electro-thermodynamic state of the mixture, occupying a region $\Omega \subset \mathbb{R}^3$ at any time t is described by the number densities n_α, the barycentric velocity $\boldsymbol{v}$ and the electrostatic potential φ.

Multiplication of the number densities n_α by m_α gives the partial mass densities

$$\rho_\alpha = m_\alpha n_\alpha. \tag{3}$$

The total number density, the (total) mass density and the free charge density are defined by

$$n = \sum_{\alpha=0}^{N} n_\alpha, \qquad \rho = \sum_{\alpha=0}^{N} m_\alpha n_\alpha, \qquad n^{\mathrm{F}} = e_0 \sum_{\alpha=0}^{N} z_\alpha n_\alpha. \tag{4}$$

The partial velocities of the species A_α are denoted by $\boldsymbol{v}_\alpha$ and $\boldsymbol{u}_\alpha = \boldsymbol{v}_\alpha - \boldsymbol{v}$ is the diffusion velocity with respect to the barycentric velocity. The barycentric velocity and the diffusion fluxes of constituents A_α are related to the partial and relative velocities by

$$\boldsymbol{v} = \frac{1}{\rho} \sum_{\alpha=0}^{N} \rho_\alpha \boldsymbol{v}_\alpha, \qquad \boldsymbol{J}_\alpha = \rho_\alpha \boldsymbol{u}_\alpha. \tag{5}$$

These definitions imply the important constraint

$$\sum_{\alpha=0}^{N} \boldsymbol{J}_\alpha = 0. \tag{6}$$

2.1 Balance equations of mass, momentum and Poisson equation

In the electrostatic approximation of Maxwell's equations, the magnetic contributions vanish and only the electric field $\boldsymbol{E} = -\nabla\varphi$ remains. In this case, Maxwell's equations reduce to the Poisson equation for the electrostatic potential φ. Moreover, the continuum model for ρ_α and $\boldsymbol{v}$ relies on the balance equations of partial masses and on the balance of momentum,

$$-\operatorname{div}((1+\chi)\varepsilon_0\nabla\varphi) = n^{\mathrm{F}}. \tag{7a}$$

$$\partial_t\rho_\alpha + \operatorname{div}(\rho_\alpha\boldsymbol{v} + \boldsymbol{J}_\alpha) = \sum_{k=1}^{M} \nu_\alpha^k m_\alpha R^k, \qquad \text{for} \qquad \alpha = 0,\dots,N, \tag{7b}$$

$$\partial_t\rho\boldsymbol{v} + \operatorname{div}(\rho\boldsymbol{v}\otimes\boldsymbol{v} - \boldsymbol{\Sigma}) = \rho\boldsymbol{b}. \tag{7c}$$

Here, $\boldsymbol{\Sigma}$ is the total stress tensor.[1] The dielectric constant is ε_0 and the dielectric susceptibility is χ. The force density, $\rho\boldsymbol{b}$, due to gravitation will be ignored.

Conservation of mass. The sum of partial mass balances implies the conservation of the total mass. By (2) and (6) we obtain

$$\partial_t\rho + \operatorname{div}(\rho\boldsymbol{v}) = 0. \tag{8}$$

Conservation of electric charge. The balance equations of partial masses yield the conservation of free electric charge

$$\partial_t n^{\mathrm{F}} + \operatorname{div}(n^{\mathrm{F}}\boldsymbol{v} + \boldsymbol{J}^{\mathrm{F}}) = 0, \tag{9}$$

where the free electric current density $\boldsymbol{J}^{\mathrm{F}}$ is defined by

$$\boldsymbol{J}^{\mathrm{F}} = \sum_{\alpha=0}^{N} \frac{z_\alpha e_0}{m_\alpha}\boldsymbol{J}_\alpha. \tag{10}$$

2.2 General constitutive equations

The balance equations are complemented by constitutive equations for the diffusion fluxes $\boldsymbol{J}_\alpha$, the reaction rates R^k and the total stress tensor $\boldsymbol{\Sigma}$. The constitutive equations are restricted by the second law of thermodynamics and some symmetry principles [1,12,19]. In [12], general constitutive equation for magnetizable, polarizable, elastic, viscous, heat conducting and reactive mixtures, which are compatible to

---

[1] The total stress tensor consists of the Cauchy and the Maxwell stress tensor. We refer to [9,12] for more details.

the second law of thermodynamics, and the Galilean symmetry principle, are derived. In the isothermal and electrostatic setting, these constitutive equations reduce to[2]

$$\boldsymbol{J}_\alpha = -\sum_{\beta=1}^{N} M_{\alpha\beta}\Big(\nabla\Big(\frac{\mu_\beta}{T}-\frac{\mu_0}{T}\Big)+\frac{1}{T}\Big(\frac{z_\beta e_0}{m_\beta}-\frac{z_0 e_0}{m_0}\Big)\nabla\varphi\Big), \qquad \text{for} \quad \alpha = 1,\dots,N, \tag{11a}$$

$$\boldsymbol{\Sigma} = -p\mathbf{1} + (1+\chi)\varepsilon_0\big(-\tfrac{1}{2}|\nabla\varphi|^2\mathbf{1} + (\nabla\varphi\otimes\nabla\varphi)\big) + \eta_b\,\mathrm{div}(\boldsymbol{v})\mathbf{1} + \eta_s\big(\nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^T\big), \tag{11b}$$

$$R^k = R_0^k\Big(\exp\Big(-\tfrac{\beta^k}{k_BT}\sum_{\alpha=0}^{N}\nu_\alpha^k m_\alpha\mu_\alpha\Big) - \exp\Big(\tfrac{(1-\beta^k)}{k_BT}\sum_{\alpha=0}^{N}\nu_\alpha^k m_\alpha\mu_\alpha\Big)\Big). \tag{11c}$$

Here, μ_α are the chemical potentials[3] and p is the material pressure. Both are defined in terms of a free energy function $\rho\psi = \rho\widetilde{\psi}(T,\rho_0,\dots,\rho_N) + \frac{1}{2}\chi\varepsilon_0|\boldsymbol{E}|^2$,

$$\mu_\alpha = \frac{\partial\rho\psi}{\partial\rho_\alpha}, \qquad\qquad p = -\rho\widetilde{\psi} + \sum_{\alpha=0}^{N}\rho_\alpha\mu_\alpha. \tag{12}$$

For simplicity we assume that the dielectric susceptibility χ is constant. The kinetic coefficients, i.e. mobilities $M_{\alpha\beta}$, bulk viscosity η_b, shear viscosity η_s and rate R_0^k, are restricted by the second law of thermodynamics such that the entropy production is non-negative,

$$M_{\alpha\beta} \quad \text{pos. def.}, \qquad \eta_s > 0, \qquad \eta_b + \tfrac{2}{3}\eta_s > 0, \qquad R_0^k > 0. \tag{13}$$

Thus, the second law of thermodynamics restricts only the sign of the kinetic coefficients, they still may be functions of the thermodynamic fields and their derivatives.

Our approach (11c) for the reaction rates is widely used in electrochemistry for surface reactions [11]. The constants β^k are called symmetry factor, which fosters either the forward or the backward reaction. From a thermodynamic point of view there is no restriction on β^k, usually $\beta \in (0,1)$ is chosen. We will not focus on the viscosity in this paper, therefore we assume that η_b, η_s are constants.

2.3 Transference numbers and ionic conductivity

Insertion of the constitutive equations (11a) for the diffusion fluxes into the relation (10) of the electric current density yields the representation

$$\boldsymbol{J}^{\mathrm{F}} = -\sigma\nabla\varphi - \sum_{\beta=1}^{N}\sigma\, t_\beta\,\frac{m_\beta}{z_\beta e_0}\nabla\Big(\mu_\beta - \mu_0\Big), \tag{14}$$

---

[2] Note, only N diffusion fluxes are specified by constitutive relations. The flux $\boldsymbol{J}_0$ is determined by the constraint (6).

[3] The chemical potentials are defined with respect to the mass densities, therefore their physical unit is J/kg. In electrochemistry, it is common to define the chemical potentials with respect to the number densities and to use the physical unit J/mol.

where the conductivity σ and the transference numbers t_β are defined by

$$\sigma = \sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} \tfrac{z_\alpha e_0}{m_\alpha}\tfrac{M_{\alpha\beta}}{T}\tfrac{z_\beta e_0}{m_\beta}, \qquad t_\beta = \frac{1}{\sigma}\sum_{\alpha=1}^{N} \tfrac{z_\alpha e_0}{m_\alpha}\tfrac{M_{\alpha\beta}}{T}\tfrac{z_\beta e_0}{m_\beta}. \tag{15}$$

Since the mobility matrix $M_{\alpha\beta}$ is positive definite, the conductivity is non-negative, i.e. $\sigma \geq 0$ and the definition of the transference numbers implies $\sum_{\beta=1}^{N} t_\beta = 1$. The relation (14) can be used to replace the electric potential by the electric current density within the diffusion fluxes (11a),[4]

$$\boldsymbol{J}_\alpha = -\sum_{\beta=1}^{N}\Big(\tfrac{M_{\alpha\beta}}{T} - \sigma\tfrac{m_\alpha}{z_\alpha e_0}\tfrac{m_\beta}{z_\beta e_0}t_\alpha t_\beta\Big)\nabla\big(\mu_\beta - \mu_0\big) + \tfrac{m_\alpha}{z_\alpha e_0}t_\alpha \boldsymbol{J}^{\mathrm{F}} \qquad \alpha = 1,\ldots,N. \tag{16}$$

In the absence of chemical potential gradients, the transference number t_α describes the fraction of the current due to the diffusion flux $\boldsymbol{J}_\alpha$ of species A_α. Recall that the diffusion fluxes $\boldsymbol{J}_\alpha$ are defined with respect to the barycentric velocity $\boldsymbol{v}$. Thus, the above defined transference numbers are related to the barycentric velocity. Other definitions of different transference numbers are possible, e.g. the use of transference numbers t_α^0 with respect to the solvent velocity $\boldsymbol{v}_0$ is quite common, cf. (Sect. 12.3 of [20]).

3 Specific constitutive modeling for liquid electrolytes

Two additional ingredients must be added to the model of the preceding section in order to obtain a complete model. These are: (i) a free energy model and (ii) a constitutive model for the kinetic coefficients.

3.1 Bulk free energy model

A suitable free energy model for liquid electrolytes in the bulk is derived and analyzed in [6,7,9,15]. Here, we give only a brief summary of its characteristic features.

The free energy density consists of three contributions: reference energies, entropy of mixing and elasticity

$$\rho\widetilde{\psi} = \rho\psi^{\mathrm{ref}} + \rho\psi^{\mathrm{mix}} + \rho\psi^{\mathrm{mech}}. \tag{17}$$

We consider an ideal mixture, i.e.

$$\rho\psi^{\mathrm{ref}}(T,\rho_0,\ldots,\rho_N) = \sum_{\alpha=0}^{N}\frac{\rho_\alpha}{m_\alpha}\psi_\alpha^{\mathrm{ref}}, \tag{18a}$$

$$\rho\psi^{\mathrm{mix}}(T,\rho_0,\ldots,\rho_N) = k_B T\sum_{\alpha=0}^{N} n_\alpha \ln\left(\frac{n_\alpha}{n}\right). \tag{18b}$$

---

[4] This representation can also formally be used if some $z_\alpha = 0$.

The mechanical part of the free energy is represented by an isotropic elastic response of a volume change,

$$\rho\psi^{\mathrm{mech}}(T,\rho_0,\dots,\rho_N) = (p^{\mathrm{ref}} - K)(n\,H - 1) + K\;n\,H\ln(nH) \text{ with } \quad nH = \sum_{\alpha=0}^{N} \upsilon_\alpha^{\mathrm{ref}} n_\alpha. \tag{19}$$

The reference energy is composed of the reference free energies $\psi_\alpha^{\mathrm{ref}}$ of each individual constituent of the mixture. In general these reference values depend on temperature, but in the isothermal setting they are assumed to be constants. The entropy of mixing accounts for the number of possible arrangements of the constituents that give rise to the same macroscopic state. In statistical thermodynamics, it is determined by means of the Boltzmann formula. The mechanical part of the free energy density is chosen such that from (12) a simple linear constitutive relation for the pressure p results, viz.

$$p = p^{\mathrm{ref}} + K(nH - 1). \tag{20}$$

The function H is the mean specific volume of the mixture and accounts for volume changes due to a local variation of the mixtures composition.

In the incompressible limit, i.e. $K \gg p^{\mathrm{ref}}$, the pressure p is an independent variable of the system and from (20) we obtain the constraint,

$$K/p^{\mathrm{ref}} \to \infty : \qquad \sum_{\alpha=0}^{N} \upsilon_\alpha^{\mathrm{ref}} n_\alpha = 1, \tag{21}$$

where $\upsilon_\alpha^{\mathrm{ref}}$ denotes the partial specific volume of the constituent A_α under the reference pressure p^{ref} and reference temperature T^{ref}. For more details on the limiting procedure, we refer to [6,9,15].

From the free energy density we obtain the chemical potentials of the constituents of the mixture,

$$K/p^{\mathrm{ref}} \to \infty : \qquad \mu_\alpha = \tfrac{1}{m_\alpha}\psi_\alpha^{\mathrm{ref}} + \tfrac{\upsilon_\alpha^{\mathrm{ref}}}{m_\alpha}p + \tfrac{k_B T}{m_\alpha}\ln\left(\frac{n_\alpha}{n}\right). \tag{22}$$

3.2 Diffusion coefficients

The second law of thermodynamics requires the matrix of the mobility coefficients $M_{\alpha\beta}$ to be positive definite, but it does not provide any dependency on partial mass densities or other thermodynamic fields. Moreover, it is not obvious how to model the mobilities with a theory on a finer scale. In the literature, diffusion of multi-component systems is often alternatively described by constitutive equations of Maxwell–Stefan type, cf. e.g. [13,18,20,24,26,27]. Relying on kinetic theory it has been observed that the dependence on the partial mass densities is much simpler for the Maxwell–Stefan diffusivities than for the mobilities. For this reason we consider in this section the Maxwell–Stefan approach to derive the mobilities $M_{\alpha\beta}$.

Alternative constitutive equations. The formulation of constitutive equations is based on a specific representation of the entropy production and the requirement of non-negative entropy production in each diffusive mechanism, cf. [12]. Based on the balance equations of the previous section and an appropriate choice of the entropy density function, the entropy production due to diffusion can be represented as

$$0 \le \xi_{\mathrm{diff}} = -\sum_{\alpha=0}^{N} \boldsymbol{J}_\alpha \cdot \nabla\big(\tfrac{\mu_\alpha^e}{T}\big) \quad \overset{(5)}{=} -\sum_{\alpha=0}^{N} \rho_\alpha \nabla\big(\tfrac{\mu_\alpha^e}{T}\big) \cdot \boldsymbol{u}_\alpha, \tag{23}$$

where the electrochemical potentials are defined as

$$\mu_\alpha^e = \mu_\alpha + \tfrac{z_\alpha e_0}{m_\alpha}\varphi. \tag{24}$$

Next we define

$$\boldsymbol{A}_\alpha = \rho_\alpha\big(\nabla\tfrac{\mu_\alpha^e}{T} + \boldsymbol{\Lambda}\big) \qquad \text{with} \qquad \rho\boldsymbol{\Lambda} = \sum_{\alpha=0}^{N} \rho_\alpha \nabla\big(\tfrac{\mu_\alpha^e}{T}\big). \tag{25}$$

This definition implies the constraint $\sum_{\alpha=0}^{N} \boldsymbol{A}_\alpha = 0$ and, together with the constraint (6), the entropy production due to diffusion can be rewritten as

$$0 \le \xi_{\mathrm{diff}} = -\sum_{\alpha=1}^{N} \boldsymbol{A}_\alpha \cdot (\boldsymbol{u}_\alpha - \boldsymbol{u}_0). \tag{26}$$

We choose linear relations between the corresponding binary factors of the entropy production, cf. [1,8,12]. and obtain the constitutive equations[5]

$$\boldsymbol{A}_\alpha = -\sum_{\beta=1}^{N} \tau_{\alpha\beta}\,(\boldsymbol{u}_\beta - \boldsymbol{u}_0), \quad \alpha = 1, \ldots, N. \tag{27}$$

The entropy production is non-negative if the kinetic coefficients $\tau_{\alpha\beta}$ define a positive definite $N \times N$ matrix.

Relations between kinetic coefficients. Because the Fick mobility matrix with the coefficients $M_{\alpha\beta}$ is positive definite, there is in particular a unique inverse matrix that is also positive definite. We denote the coefficients of this inverse matrix by $B_{\alpha\beta}$. Thus, we can rewrite (11a) as

$$\sum_{\beta=1}^{N} B_{\alpha\beta} \boldsymbol{J}_\beta = -\nabla\big(\tfrac{\mu_\alpha^e}{T} - \tfrac{\mu_0^e}{T}\big), \quad \alpha = 1, \ldots, N. \tag{28}$$

Next we determine the coefficients $B_{\alpha\beta}$ as function of $\tau_{\alpha\beta}$, for this purpose we define for $\alpha, \beta = 1, \ldots, N$

$$\widetilde{\tau}_{\alpha\beta} := \tau_{\alpha\beta}, \qquad \widetilde{\tau}_{\alpha 0} := -\sum_{\beta=1}^{N} \tau_{\alpha\beta}, \qquad \widetilde{\tau}_{0\beta} := -\sum_{\alpha=1}^{N} \tau_{\alpha\beta}, \qquad \widetilde{\tau}_{00} := \sum_{\alpha,\beta=1}^{N} \tau_{\alpha\beta}. \tag{29}$$

---

[5] The form (11a) of the diffusive fluxes $\boldsymbol{J}_{\boldsymbol{\alpha}}$ was analogously obtained from the first expression for ξ_{diff} in (23) by applying the constraint (6) and linear relations between the binary factors.

The definition directly implies the constraint

$$\sum_{\beta=0}^{N} \widetilde{\tau}_{\alpha\beta} = 0, \tag{30}$$

and we can rewrite the constitutive equation (27) as

$$\boldsymbol{A}_\alpha \overset{(29)}{=} -\sum_{\beta=0}^{N} \widetilde{\tau}_{\alpha\beta}\, \boldsymbol{u}_\beta = -\sum_{\beta=0}^{N} \frac{\widetilde{\tau}_{\alpha\beta}}{\rho_\beta} \boldsymbol{J}_\beta, \qquad \alpha = 0, \ldots, N. \tag{31}$$

Subtracting the equation for $\alpha = 0$ from the remaining equations, we obtain

$$\begin{aligned} \nabla\big(\tfrac{\mu_\alpha^e}{T} - \tfrac{\mu_0^e}{T}\big) \overset{(25)}{=} \frac{\boldsymbol{A}_\alpha}{\rho_\alpha} - \frac{\boldsymbol{A}_0}{\rho_0} &= -\sum_{\beta=0}^{N} \Big(\frac{\widetilde{\tau}_{\alpha\beta}}{\rho_\alpha\rho_\beta} - \frac{\widetilde{\tau}_{0\beta}}{\rho_0\rho_\beta}\Big) \boldsymbol{J}_\beta \\ &\overset{(29)}{=} -\sum_{\beta=1}^{N} \Big(\frac{\widetilde{\tau}_{\alpha\beta}}{\rho_\alpha\rho_\beta} - \frac{\widetilde{\tau}_{0\beta}}{\rho_0\rho_\beta} - \frac{\widetilde{\tau}_{\alpha0}}{\rho_\alpha\rho_0} + \frac{\widetilde{\tau}_{00}}{\rho_0\rho_0}\Big) \boldsymbol{J}_\beta. \end{aligned} \tag{32}$$

By comparison with (28) we identify

$$B_{\alpha\beta} = \frac{\widetilde{\tau}_{\alpha\beta}}{\rho_\alpha\rho_\beta} - \frac{\widetilde{\tau}_{0\beta}}{\rho_0\rho_\beta} - \frac{\widetilde{\tau}_{\alpha0}}{\rho_\alpha\rho_0} + \frac{\widetilde{\tau}_{00}}{\rho_0\rho_0}. \tag{33}$$

Maxwell–Stefan setting. Maxwell–Stefan diffusion laws are most commonly written in the form[6]

$$\rho_\alpha \,(\nabla \tfrac{\mu_\alpha^e}{T} - \boldsymbol{\Lambda}) = \sum_{\beta=0}^{N} \widetilde{\tau}_{\alpha\beta}\, (\boldsymbol{u}_\alpha - \boldsymbol{u}_\beta), \tag{34}$$

which follows from (31) by applying (25) and (29). The constitutive modeling now consists in specifying how the coefficients $\widetilde{\tau}_{\alpha\beta}$ for $\alpha \neq \beta$ depend on ρ_α for $\alpha = 0, \ldots, N$. In the Maxwell–Stefan theory, it is assumed that $\widetilde{\tau}_{\alpha\beta}$ is approximately proportional to the mass densities ρ_α and ρ_β. We introduce so called *friction factors* $f_{\alpha\beta}$ and the *Maxwell–Stefan diffusivities* $\mathcal{D}_{\alpha\beta}$ as follows,

$$\widetilde{\tau}_{\alpha\beta} = -f_{\alpha\beta}\, \rho_\alpha\rho_\beta \quad = -\frac{k_B}{n} \frac{n_\alpha n_\beta}{\mathcal{D}_{\alpha\beta}} \qquad \text{for } \alpha \neq \beta. \tag{35}$$

In the following, we assume constant Maxwell–Stefan diffusivities $\mathcal{D}_{\alpha\beta}$. The friction factors and the Maxwell–Stefan diffusivities are related by

$$f_{\alpha\beta} = \frac{k_B}{n} \frac{1}{m_\beta m_\alpha} \frac{1}{\mathcal{D}_{\alpha\beta}} \qquad \text{for } \alpha \neq \beta. \tag{36}$$

---

[6] Considering only the quasi-equilibrium of the momentum balance (7c), i.e. $\nabla p = -n^{\mathrm{F}} \nabla\varphi$, implies for an isothermal process $\rho\Lambda = \sum_{\alpha=0}^{N} \rho_\alpha \nabla \frac{\mu_\alpha^e}{T} = 0$. Then, (34) coincides with the textbook literature, cf. e.g. [Eq. (12.1) of [20]].

The specific dependency on the number densities of $\widetilde{\tau}_{\alpha\beta}$ implies that $\widetilde{\tau}_{\alpha\beta}$ is symmetric, see [1,28]. The symmetry of the mobility matrix $M_{\alpha\beta}$ and its inverse matrix $B_{\alpha\beta}$ then follows by (33). Starting from (26) and (27) and applying (29) multiple times, we obtain for the entropy production due to diffusion, cf. [1,28],

$$\begin{aligned} 0 < \xi_{\text{diff}} &= \sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} \tau_{\alpha\beta}\,(\boldsymbol{u}_\beta - \boldsymbol{u}_0)\cdot(\boldsymbol{u}_\alpha - \boldsymbol{u}_0) = \sum_{\beta=1}^{N}(\boldsymbol{u}_\beta - \boldsymbol{u}_0)\cdot\sum_{\alpha=0}^{N}\widetilde{\tau}_{\alpha\beta}\,\boldsymbol{u}_\alpha \\ &= \sum_{\alpha=0}^{N}\boldsymbol{u}_\alpha\cdot\sum_{\beta=0}^{N}\widetilde{\tau}_{\alpha\beta}\,\boldsymbol{u}_\beta = -\frac{1}{2}\sum_{\alpha=0}^{N}\sum_{\beta=0}^{N}\widetilde{\tau}_{\alpha\beta}(\boldsymbol{u}_\alpha - \boldsymbol{u}_\beta)^2. \end{aligned} \tag{37}$$

Positivity of ξ_{diff} for all possible $\boldsymbol{u}_\alpha$ and $\boldsymbol{u}_\beta$ thus requires $\widetilde{\tau}_{\alpha\beta} < 0$ for $\alpha, \beta = 0, \ldots, N$ with $\alpha \neq \beta$. This, together with the symmetry of $\widetilde{\tau}_{\alpha\beta}$, implies for the friction factors $f_{\alpha\beta}$ and the Maxwell–Stefan diffusivities $\mathcal{D}_{\alpha\beta}$

$$f_{\alpha\beta} = f_{\beta\alpha} > 0 \quad \text{for } \alpha \neq \beta \quad \text{or equivalently} \;\; \mathcal{D}_{\alpha\beta} = \mathcal{D}_{\beta\alpha} > 0 \quad \text{for} \;\; \alpha \neq \beta. \tag{38}$$

Mobility coefficients. Applying the definition (29) and the Maxwell–Stefan form (35) of the coefficients $\widetilde{\tau}_{\alpha\beta}$, we obtain for $\alpha = 1, \ldots, N$

$$\begin{aligned} B_{\alpha\alpha} &= \frac{\widetilde{\tau}_{\alpha\alpha}}{\rho_\alpha\rho_\alpha} - \frac{\widetilde{\tau}_{0\alpha}}{\rho_0\rho_\alpha} - \frac{\widetilde{\tau}_{\alpha 0}}{\rho_\alpha\rho_0} + \frac{\widetilde{\tau}_{00}}{\rho_0\rho_0} = -\sum_{\gamma\neq\alpha}\frac{\tau_{\gamma\alpha}}{\rho_\alpha\rho_\alpha} - 2\frac{\tau_{0\alpha}}{\rho_0\rho_\alpha} - \sum_{\gamma\neq 0}\frac{\tau_{0\gamma}}{\rho_0\rho_0} \\ &= \frac{k_B}{n}\left(\sum_{\gamma\neq\alpha}\frac{\rho_\gamma}{\rho_\alpha}\frac{1}{m_\gamma m_\alpha\mathcal{D}_{\gamma\alpha}} + 2\frac{1}{m_0 m_\alpha\mathcal{D}_{0\alpha}} + \sum_{\gamma\neq 0}\frac{\rho_\gamma}{\rho_0}\frac{1}{m_0 m_\gamma\mathcal{D}_{0\gamma}}\right) \\ &= \frac{k_B}{n}\left(\frac{\rho_0}{\rho_\alpha}\frac{(1+\frac{\rho_\alpha}{\rho_0})^2}{m_0 m_\alpha\mathcal{D}_{0\alpha}} + \sum_{\gamma\neq 0,\alpha}\frac{\rho_\gamma}{\rho_\alpha}\frac{1}{m_\gamma m_\alpha\mathcal{D}_{\gamma\alpha}} + \frac{\rho_\gamma}{\rho_0}\frac{1}{m_0 m_\gamma\mathcal{D}_{0\gamma}}\right), \end{aligned} \tag{39a}$$

and for $\alpha \neq \beta$ we have

$$\begin{aligned} B_{\alpha\beta} &= \frac{\widetilde{\tau}_{\alpha\beta}}{\rho_\alpha\rho_\beta} - \frac{\widetilde{\tau}_{0\beta}}{\rho_0\rho_\beta} - \frac{\widetilde{\tau}_{\alpha 0}}{\rho_\alpha\rho_0} + \frac{\widetilde{\tau}_{00}}{\rho_0\rho_0} = \frac{\tau_{\alpha\beta}}{\rho_\alpha\rho_\beta} - \frac{\tau_{0\beta}}{\rho_0\rho_\beta} - \frac{\tau_{\alpha 0}}{\rho_\alpha\rho_0} - \sum_{\gamma\neq 0}\frac{\tau_{0\gamma}}{\rho_0\rho_0} \\ &= \frac{k_B}{n}\left(-\frac{1}{m_\alpha m_\beta\mathcal{D}_{\alpha\beta}} + \frac{1}{m_0 m_\beta\mathcal{D}_{0\beta}} + \frac{1}{m_\alpha m_0\mathcal{D}_{\alpha 0}} + \sum_{\gamma\neq 0}\frac{\rho_\gamma}{\rho_0}\frac{1}{m_0 m_\gamma\mathcal{D}_{0\gamma}}\right). \end{aligned} \tag{39b}$$

4 Discussion of two limiting cases

For further characterization of the continuum model and to relate it to the literature, we discuss two limiting situations. Let us consider an incompressible mixture, where A_0 denotes the uncharged solvent of the mixture, i.e. $z_\alpha = 0$. Insertion of the chemical potentials (22) into the diffufluxes (11a) yields an explicit expression for the diffusion fluxes

$$\begin{aligned}\boldsymbol{J}_\alpha = -k_B T\, m_\alpha \sum_{\beta=1}^{N} \frac{M_{\alpha\beta}}{T m_\alpha m_\beta n_\beta} \\ \times\Big(\nabla n_\beta + n_\beta \frac{z_\beta e_0}{k_B T}\nabla\varphi + \frac{n_\beta}{n_0}\Big[-\frac{m_\beta}{m_0}\nabla n_0 - \frac{n_0}{n}\Big(1-\frac{m_\beta}{m_0}\Big)\nabla n \\ + \frac{n_0}{k_B T}\Big(v_\beta^{\mathrm{ref}} - \frac{m_\beta}{m_0} v_0^{\mathrm{ref}}\Big)\nabla p\Big]\Big).\end{aligned} \tag{40}$$

Compared to the standard Nernst–Planck model, cf. [2,20], there are three additional terms inside the square brackets. The first term represents the solvent–ion interaction, the second one takes into account the different size of the constituents and the third term represents the coupling of pressure and diffusion fluxes.

4.1 Dilute solution theory

In the dilute solution limit, the number density of the solvent is assumed to be large compared to those of all remaining species, i.e. $n_\alpha \ll n_0$ for $\alpha = 1, \ldots, N$.

Mobility matrix. To study the mobility matrix $M_{\alpha\beta}$ in the dilute solution limit, we first analyze the dependency of the inverse matrix on the species densities. We infer from (39) that in the strong dilution limit the diagonal elements grow proportional to number densities of the respective constituents, whereas the non-diagonal elements stay bounded, i.e.

$$\frac{\rho_\alpha}{\rho_0} B_{\alpha\alpha} \to \frac{k_B}{n} \frac{1}{m_0 m_\alpha \mathcal{D}_{0\alpha}} \qquad \text{for } \frac{\rho_\alpha}{\rho_0} \to 0 \tag{41a}$$

$$\frac{\rho_\alpha}{\rho_0} B_{\alpha\beta} \to 0 \qquad \text{for } \frac{\rho_\alpha}{\rho_0} \to 0 \text{ and } \alpha \neq \beta \tag{41b}$$

and conclude for the mobility matrix

$$M_{\alpha\alpha} \to n_\alpha \frac{n}{n_0} \frac{m_\alpha^2 \mathcal{D}_{0\alpha}}{k_B} \qquad \text{for } \frac{n_\alpha}{n_0} \to 0 \tag{42a}$$

$$M_{\alpha\beta} \to 0 \qquad \text{for } \frac{n_\alpha}{n_0} \to 0 \text{ and } \alpha \neq \beta. \tag{42b}$$

In the strong dilution limit, the mobility matrix is diagonal and thus cross diffusion is negligible in this regime.

Nernst–Planck fluxes. Since $n \to n_0$ for $\frac{n_\alpha}{n_0} \to 0$, the diagonal entries in (42) simplify to

$$M_{\alpha\alpha} \to n_\alpha \frac{m_\alpha^2 \mathcal{D}_{0\alpha}}{k_B} \qquad \text{for } \frac{n_\alpha}{n_0} \to 0. \tag{43}$$

Insertion of the mobility matrix (43) into the diffusion fluxes (40), then directly yields the classical Nernst–Planck fluxes

$$\boldsymbol{J}_\alpha = -m_\alpha \mathcal{D}_{0\alpha}\Big(\nabla n_\alpha + n_\alpha \tfrac{z_\alpha e_0}{k_B T}\nabla\varphi\Big). \tag{44}$$

We conclude that under strong dilution conditions a volume exclusion mechanism is not required in an electrolyte model. However, if the Nernst–Planck flux is inappropriately applied inside electrochemical double layers, then the absence of such a volume exclusion mechanism allows unphysical, almost infinite accumulation of ions, as it is well known for the classical Poisson–Nernst–Planck model, cf. e.g. [9,14].

Conductivity and transference numbers. In the dilute solution limit, conductivity and transference numbers reduce to

$$\sigma = \sum_{\alpha=1}^{N}(z_\alpha e_0)^2 \frac{n_\alpha \mathcal{D}_{0\alpha}}{k_B T}, \qquad t_\alpha = \frac{(z_\alpha e_0)^2}{\sigma}\frac{n_\alpha \mathcal{D}_{0\alpha}}{k_B T}. \tag{45}$$

We conclude that in dilute solutions the transference numbers are always positive.

4.2 Electroneutral bulk transport

Writing the Poisson equation (7a) in dimensionless form with $\varphi = \frac{k_B T}{e_0}\widetilde{\varphi}$ and $n^{\mathrm{F}} = e_0 n^{\mathrm{ref}}\,\widetilde{n}^{\mathrm{F}}$ yields

$$-\lambda^2 \Delta\widetilde{\varphi} = \widetilde{n}^{\mathrm{F}} \qquad \text{with} \qquad \lambda L^{\mathrm{ref}} = \sqrt{\frac{(1+\chi)\varepsilon_0 k_B T}{e_0^2 n^{\mathrm{ref}}}}. \tag{46}$$

Here, L^{ref} and n^{ref} denote reference values for the size of the considered system and the electrolyte concentration, respectively. Given typical values $L^{\mathrm{ref}} = 1\,\mathrm{cm}$, $n^{\mathrm{ref}} = 1\,\mathrm{mol/L}$, we find that $\lambda \approx 10^{-9}$ is an extremely small parameter. Thus, the left hand side of the Poisson equation (46) is close to zero. Then, the Poisson equation (7a) can be replaced by the electroneutrality condition

$$\lambda \to 0: \qquad 0 = n^{\mathrm{F}}. \tag{47}$$

Thus, here the Poisson equation does not(!) reduce to the Laplace equation but to the algebraic equation (47). Note, this approximation does not hold in charged boundary layers at surfaces, where the electric field $\nabla\varphi$ changes strongly. A detailed asymptotic derivation and discussion of the electroneutrality condition and the handling of the boundary charged layers are given in [10].

Mechanical quasi-equilibrium. For simplicity we consider a quasi-equilibrium version of the momentum balance (7c),

$$\text{vanishing viscosity:} \qquad \nabla p = -n^{\mathrm{F}}\,\nabla\varphi. \tag{48}$$

The term on the right hand side is the electrostatic approximation of the Lorentz force. In the electrical double layer, where charge accumulates and electric potential drops in the order of several volts per nm, a large pressure gradient is generated. But in the electroneutral bulk region, the pressure gradient vanishes and we can set

$$p = p^{\mathrm{ref}} \qquad \text{in the bulk with } n^{\mathrm{F}} = 0. \tag{49}$$

Bulk diffusion flux of concentrated solutions. In the bulk, the diffusion fluxes (40) simplify to

$$\boldsymbol{J}_\alpha = -\, k_B T\, m_\alpha \sum_{\beta=1}^{N} \frac{M_{\alpha\beta}}{T m_\alpha m_\beta n_\beta} \left(\nabla n_\beta + n_\beta\, \tfrac{z_\beta e_0}{k_B T} \nabla \varphi - \tfrac{m_\beta}{m_0} \frac{n_\beta}{n_0} \nabla n_0 \;-\; \big(1 - \tfrac{m_\beta}{m_0}\big) \frac{n_\beta}{n} \nabla n \right), \tag{50}$$

where the last two terms describe the non-ideality of a concentrated solution in an explicit way.

5 Transport coefficients of concentrated solutions

Bulk transport properties for concentrated solutions are well described in (Sect. 12 of [20]). In this section, we investigate how the transport parameters are influenced by

- solvation of ions,
- incomplete dissociation of the neutral salt.

We consider an electrolyte that is prepared by dissolving some neutral salt A_E in a neutral solvent A_0, such that the salt dissociates into anions and cations. Many solvents, in particular in water, have a molecular structure that gives rise to microscopic dipoles. These dipoles cause a microscopic electrostatic interaction between solvent and charged ions. This interaction leads to clustering of solvent molecules around a center ion, which is known as solvation. The solvation has a profound impact on the mixing entropy within the electrolyte model [6]. Solvent molecules that are bounded by an ion do not participate in the entropic interaction with the other constituents of the electrolytic mixture. Therefore, we choose as the constituents of the mixture the solvated ions consisting of the center ion and its solvation shell and refer to the solvated anions and cations as A_- and A_+, respectively. Moreover, bounded solvent molecules move with the velocity of the center ion and contribute mass to the ionic constituent. Both effects have an impact on the barycentric velocity.

The dissociation reaction is accompanied by a solvation reaction and we write the net reaction as

$$\mathrm{A}_E + (\nu_-\kappa_- + \nu_+\kappa_+)\mathrm{A}_0 \rightleftharpoons \nu_-\mathrm{A}_- + \nu_+\mathrm{A}_+, \tag{51}$$

where κ_- and κ_+ are the numbers of solvent molecules in the solvation shell of A_- and A_+, respectively. The total amount of salt molecules within the electrolyte is given by the salt concentration,

$$c = n_E + \frac{1}{2}\left(\frac{n_+}{\nu_+} + \frac{n_-}{\nu_-}\right). \tag{52}$$

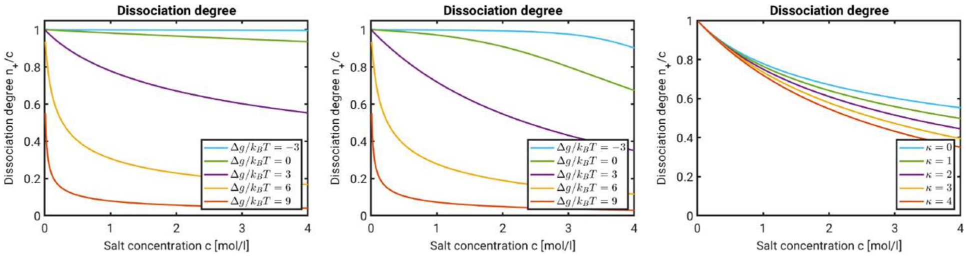

Fig. 1. Partial dissociation of a salt with $\upsilon_E^{\mathrm{ref}} = 2\upsilon_0^{\mathrm{ref}}$ and $\upsilon_\pm^{\mathrm{ref}} = (\kappa+1)\upsilon_0^{\mathrm{ref}}$. Dissociation degree for different values of the dissociation energy Δg and no solvation of ions, i.e. $\kappa = 0$ (left) and solvated ions with $\kappa_- = \kappa_+ = \kappa = 4$ (middle). Right: dissociation degree for fixed $\Delta g = 3k_BT$ and varying κ.

We assume fast dissociation and study the limit $R_0 \to \infty$, such that the reaction is in local equilibrium. From the constitutive equation (11c) we get

$$m_E\mu_E + (\nu_-\kappa_- + \nu_+\kappa_+)m_0\mu_0 = \nu_-m_-\mu_- + \nu_+m_+\mu_+, \tag{53}$$

where the chemical potentials are given by (22). Moreover in fast dissociation limit $R_0 \to \infty$ the reaction rate R is not determined by the constitutive equation (11c) anymore and becomes a new unknown of the system, which is determined by one of the mass balances. This strategy to simplify the equation system is considered e.g. in [4,21].

The amount of dissociated salt is controlled by the dissociation energy

$$\Delta g = \sum_{\alpha\in\{0,+,-,E\}} \nu_\alpha(\psi_\alpha^{\mathrm{ref}} + \upsilon_\alpha^{\mathrm{ref}} p^{\mathrm{ref}}). \tag{54}$$

Equation (53) implies for $\Delta g \to -\infty$ the salt is completely dissociated, see Figure 1.

We ignore the viscosity, i.e. $\eta_b = 0$ and $\eta_s = 0$, such that the momentum balance reduces to (48). Since we are only interested in ion transport within the bulk far away from charged boundaries, we assume that the electrolyte is locally electroneutral,

$$z_-n_- + z_+n_+ = 0. \tag{55}$$

Electroneutrality of the reaction (51) implies

$$z_-\nu_- + z_+\nu_+ = 0 \qquad \text{and with (55)} \qquad \frac{n_-}{\nu_-} = \frac{n_+}{\nu_+}. \tag{56}$$

According to Section 4.2, the pressure is constant in the bulk and is determined by the outer pressure such that $p = p^{\mathrm{ref}}$.

5.1 Electrolyte with completely dissociated salt

Assuming complete dissociation, we consider the electrolyte consisting of A_0 and the solvated ions A_+ and A_-, but there is no remaining undissociated neutral salt A_E. We define the salt mass fraction as

$$\omega_\infty = \tfrac{1}{\rho}(\rho_- + \rho_+). \tag{57}$$

The constraints of local electroneutrality (55) and incompressibility (21) allow to express the partial mass densities ρ_α and the chemical potentials as functions of the salt mass fraction ω_∞,

$$\rho_\alpha = \hat{\rho}_\alpha(\omega_\infty), \qquad \mu_\alpha = \hat{\mu}_\alpha(\omega_\infty), \qquad \text{for} \qquad \alpha \in \{+,-,0\}. \tag{58}$$

From the balance equations of mass (7b) together with the diffusion fluxes (16) we obtain a balance equation for the salt mass fraction

$$\rho\big(\partial_t \omega_\infty + \boldsymbol{v} \cdot \nabla \omega_\infty\big) = \operatorname{div}\big(\rho D\, \nabla \omega_\infty\big) - \frac{\nu_- m_- + \nu_+ m_+}{\nu_+ z_+ e_0} \boldsymbol{J}^{\mathrm{F}} \cdot \nabla t_+, \tag{59}$$

where the *salt diffusion coefficient* is defined by

$$D = \frac{1}{\rho} \sum_{\alpha,\beta \in \{+,-\}} \Big(\frac{M_{\alpha\beta}}{T} - \sigma \frac{m_\alpha}{z_\alpha e_0} \frac{m_\beta}{z_\beta e_0} t_\alpha t_\beta \Big) \frac{d(\mu_\beta - \mu_0)}{d\omega_\infty}. \tag{60}$$

The introduction of the salt mass fraction has the advantage that for an electrolytic solution, where (i) the total mass density is almost constant, (ii) the barycentric velocity vanishes and (iii) no electric current flows, the equation (59) reduces to a simple diffusion equation for the salt concentration,

$$\partial_t c = \operatorname{div}(D \nabla c). \tag{61}$$

In experimental studies, this diffusion equation is used to determine the salt diffusion coefficient D.

Motivated by (53), we define the chemical potential of the neutral salt as

$$m_E \mu_E = \nu_- m_- \mu_- + \nu_+ m_+ \mu_+ - (\nu_- \kappa_- + \nu_+ \kappa_+) m_0 \mu_0. \tag{62}$$

From the structure of the chemical potential (22), the Gibbs–Duhem relation in the right hand side of (12) and the vanishing pressure gradient $\nabla p = 0$, we obtain relations between the chemical potentials

$$\frac{d m_\pm \mu_\pm}{d\omega_\infty} = \frac{n_0}{(\nu_+ + \nu_-) n_0 + (\nu_+ \kappa_+ + \nu_- \kappa_-)(n_+ + n_-)} \frac{d m_E \mu_E}{d\omega_\infty}, \tag{63a}$$

$$\frac{d m_0 \mu_0}{d\omega_\infty} = -\frac{(n_+ + n_-)}{(\nu_+ + \nu_-) n_0 + (\nu_- \kappa_+ + \nu_+ \kappa_-)(n_+ + n_-)} \frac{d m_E \mu_E}{d\omega_\infty}. \tag{63b}$$

A direct calculation then yields for the salt diffusion coefficient

$$\begin{aligned} D &= (z_+ - z_-)\, \mathcal{F}\, \frac{\rho^2 z_+ e_0^2}{m_-^2 m_+^2 \rho_0^2 n_-} \frac{k_B \det(M)}{T\sigma}, \qquad \text{with} \\ \mathcal{F} &= \frac{\rho_0^2(\rho_+ + \rho_-)}{\rho^3 m_- m_0} \frac{(m_+ + m_-) z_- \rho_0 + m_-(z_- m_+ - z_+ m_-)(n_+ + n_-)}{(\nu_+ + \nu_-) n_0 + (\nu_+ \kappa_+ + \nu_- \kappa_-)(n_+ + n_-)} \frac{1}{k_B T} \frac{d m_E \mu_E}{d\omega_\infty}. \end{aligned} \tag{64}$$

Here, the so-called thermodynamic factor $\mathcal{F}$ is introduced, which is independent of the Maxwell–Stefan diffusivities. Finally, we use the representations (39) for the inverse of the mobility matrix to obtain explicit representations for the transference

Table 2. Material parameters used in the numerical examples.

$z_+ = 1$	$z_- = -1$	$\nu_\pm = 1$
$\upsilon_0^{\mathrm{ref}} = 0.0182\,\mathrm{L/mol}$	$\upsilon_-^{\mathrm{ref}} = (\kappa+1)\,\upsilon_0^{\mathrm{ref}}$	$\upsilon_+^{\mathrm{ref}} = (\kappa+1)\,\upsilon_0^{\mathrm{ref}}$
$\upsilon_E^{\mathrm{ref}} = 2\upsilon_0^{\mathrm{ref}}$	$m_- = (\kappa+1)\,m_0$	$m_+ = (\kappa+1)\,m_0$

number, conductivity and salt diffusion coefficient in terms of the Maxwell–Stefan diffusivities,

$$t_+ = \frac{\rho_0}{\rho}\frac{z_+\mathcal{D}_{0+}}{z_+\mathcal{D}_{0+} - z_-\mathcal{D}_{0-}} + \frac{\rho_-}{\rho}, \tag{65a}$$

$$D = \frac{n}{n_0}\mathcal{F}\left(\frac{\mathcal{D}_{0+}\mathcal{D}_{0-}(z_+ - z_-)}{z_+\mathcal{D}_{0+} - z_-\mathcal{D}_{0-}}\right), \tag{65b}$$

$$\frac{1}{\sigma} = \frac{k_B T}{-z_- z_+ e_0^2}\frac{1}{n}\left(\frac{1}{\mathcal{D}_{+-}} + \frac{n_0}{n_-}\frac{z_+}{z_+\mathcal{D}_{0+} - z_-\mathcal{D}_{0-}}\right). \tag{65c}$$

The conductivity σ, transference number t_+ are expectable in full agreement with (Sect. 12 of [20]) because they do not directly depend on the free energy model, i.e. on the chemical potentials. Also the dependence of D on the Maxwell–Stefan diffusivities in (65b) agrees with (Sect. 12 of [20]), but the coincidence of the thermodynamic factor is not obvious and depends on the considered potentials. We observe in (65) that at any salt concentration the three Maxwell–Stefan diffusivities $\mathcal{D}_{0+}$, $\mathcal{D}_{0-}$ and $\mathcal{D}_{+-}$ can be uniquely determined from the three transport parameters t_+, D and σ, but only the conductivity depends on the coefficient $\mathcal{D}_{+-}$. In the dilute solution limit, this dependence of σ on the ion–ion interaction vanishes.

To study the transport parameters (65), we introduce a mean value $\bar{\mathcal{D}}$ of the Maxwell–Stefan diffusion coefficients and the molar conductivity Λ as

$$\bar{\mathcal{D}} := \frac{z_+\mathcal{D}_{0+} - z_-\mathcal{D}_{0-}}{z_+ - z_-} \qquad \Lambda := \frac{e_0^2}{k_B T}\sum_{\alpha=+,-} z_\alpha^2 \nu_\alpha \mathcal{D}_{0\alpha}. \tag{66}$$

Then the salt diffusion coefficient and the conductivity are normalized with respect to $\bar{\mathcal{D}}$ and Λ, respectively. Thus, the normalized quantities depend only on the fractions $\mathcal{D}_{+-}/\bar{\mathcal{D}}$ and $\mathcal{D}_{0\pm}/\bar{\mathcal{D}}$. We use the material parameters defined in Table 2 to describe a monovalent binary electrolyte. We assume that cations and anions are solvated by the same number κ of solvent molecules.

Electrolytes without ion solvation. To describe electrolytes consisting only of free solvent molecules and unsolvated ions, we set in (51) $\kappa_- = \kappa_+ = 0$. Keeping $\bar{\mathcal{D}}$ and Λ fixed, we observe in Figure 2 that the conductivity σ is – as expected from (65c) with fixed $\bar{\mathcal{D}}$ – independent of the ratio $\mathcal{D}_{0+}$ and $\mathcal{D}_{0-}$ and monotone increasing with the salt concentration c. For low salt concentrations σ is already fully determined by Λ, while for higher salt concentrations the influence of $\mathcal{D}_{+-}$ increases, leading to a less than linear growth of σ with respect to c, if $\mathcal{D}_{+-} < \bar{\mathcal{D}}$, see Figure 3.

Increasing the ratio $\mathcal{D}_{0+}/\mathcal{D}_{0-}$ leads to a larger fraction of the current being carried by the cations. Thus, the transference number changes proportional to D_{0+}/D_{0-}. We

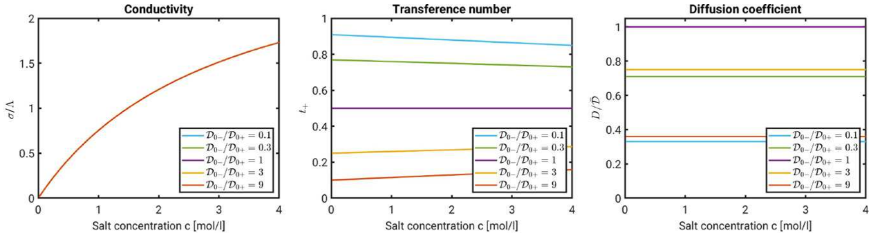

Fig. 2. Transport parameters for different ratios of $\mathcal{D}_{0-}/\mathcal{D}_{0+}$ and fixed $\bar{\mathcal{D}}$. Conductivity σ (left), cation transference number t_+ (middle) and salt diffusion coefficient (right) with respect to the salt concentration c. The remaining parameters are $\kappa = 0$ and $\mathcal{D}_{+-} = \bar{\mathcal{D}}/10$.

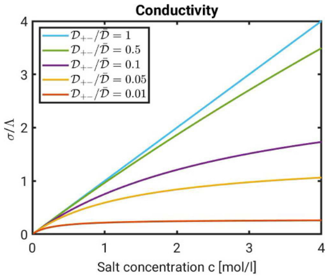

Fig. 3. Impact of $\mathcal{D}_{+-}$ on the conductivity σ for $\kappa = 0$.

observe only a small impact of the salt concentration on the transference numbers.[7] For increasing c, the transference numbers tend to limit value 1/2.

For the given choice of parameters the diffusion coefficient D shows almost no dependence on the salt concentration. A variation of $\mathcal{D}_{0+}/\mathcal{D}_{0-}$ leads to a shift of D, whereby the largest value is obtained for equal diffusivities $\mathcal{D}_{0+} = \mathcal{D}_{0-}$.

Keeping $\mathcal{D}_{0+}$ and $\mathcal{D}_{0-}$ fixed and varying $\mathcal{D}_{+-}$, the resulting curves of t_+ and D are unchanged as in Figure 2 only the conductivity depends on $\mathcal{D}_{+-}$ as shown in Figure 3, as expected from (65).

Impact of solvation number κ. Ion solvation leads to an increase of the specific volume and molar mass of the ionic species, compared to the unsolvated ions. As a simple approximation we assume that $\kappa_+ = \kappa_- = \kappa$ and the mass and the specific volume of the solvated ions are given by

$$m_\alpha = (z_\alpha \kappa + 1) m_0, \qquad v_\alpha^{\mathrm{ref}} = (z_\alpha \kappa + 1) v_0^{\mathrm{ref}} \tag{67}$$

for $\alpha \in \{+, -\}$. In a mixture where the constituents are solvated ions, the total number density n is lower than in the corresponding cases, where the ionic species are represented by center ions without the solvation shell. Therefore, increasing the solvation number κ decreases the total number density n. According to (65) we have to expect an influence of the solvation number κ on all transport parameters.[8]

Nevertheless, the salt diffusion coefficient is almost constant $D \approx \bar{\mathcal{D}}$ as before and almost unaffected by the solvation number. However, the conductivity depends strongly on the solvation number for high salt concentrations, see Figure 4 left. Larger values of κ lowers the conductivity. In particular, for $\kappa > 2$, the conductivity becomes

---

[7] The transference number t_+^0 with respect to the solvent velocity is independent of the salt concentration and is given by the values of t_+ for $c = 0$.

[8] See footnote 7.

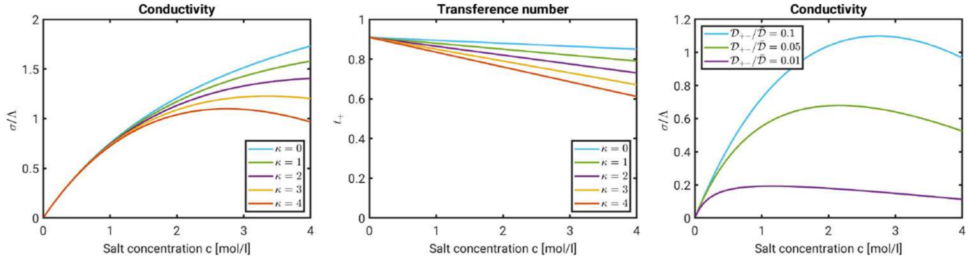

Fig. 4. Impact solvation solvation number κ on the conductivity σ (left) and transference number t_+ (middle) for fixed $\mathcal{D}_{+-} = \bar{\mathcal{D}}/10$. Conductivity for fixed $\kappa = 4$ and variation of $\mathcal{D}_{+-}$ (right). The remaining parameter is $\mathcal{D}_{0-} = \mathcal{D}_{0+}/10$.

non-monotone with respect to c, leading to the well-known parabolic shape of σ for aqueous electrolytes [29]. A reduction of the ion–ion diffusion coefficient $\mathcal{D}_{+-}$ leads to a further decrease of the conductivity and the maximum is attained at lower salt concentration, shown in Figure 4 right. For unequal ion–solvent diffusion coefficients the transference numbers are almost linear and for larger solvation numbers t_+ increases its slope, see Figure 4 middle.

5.2 Electrolyte with incomplete dissociated salt

To describe incomplete dissociation, we consider a mixture of four constituents: the solvent A_0, the possibly solvated ions A_+ and A_- and the neutral salt A_E. Thus, in addition to the three diffusivities $\mathcal{D}_{0+}$, $\mathcal{D}_{0-}$ and $\mathcal{D}_{+-}$, three further diffusivities occur, denoted by $\mathcal{D}_{E+}$, $\mathcal{D}_{E-}$ and $\mathcal{D}_{E0}$. Nevertheless, in the fast dissociation regime the imposed constraints of local electroneutrality (55) and of incompressiblity (21) still allow a characterization of the electrolyte by the three transport parameter conductivity σ and transference number t_+ according to (15) and a salt diffusion coefficient D defined below in (72).

Similar to the case of complete dissociation, we define the salt mass fraction as

$$\omega_e = \frac{1}{\rho}\left(\rho_- + \rho_+ + \frac{\nu_- m_- + \nu_+ m_+}{m_E}\rho_E\right). \tag{68}$$

Again, the local electroneutrality (55), the incompressiblity constraint (21) and in addition now the fast reaction assumption (53) allow to express all number densities ρ_α and chemical potentials as functions of the salt mass fraction ω_e. Moreover, from the mass balance equations (7b) we obtain a balance equation for the salt mass fraction ω_e,

$$\rho\big(\partial_t \omega_e + \boldsymbol{v}\cdot\nabla\omega_e\big) + \operatorname{div}\left(\sum_{\alpha\in\{+,-\},E} \delta_\alpha \boldsymbol{J}_\alpha\right) = 0, \tag{69}$$

where δ_α is defined as

$$\delta_\alpha = \begin{cases} 1 & \text{for} \quad \alpha\in\{+,-\} \\ \frac{\nu_- m_- + \nu_+ m_+}{m_E} & \text{for} \quad \alpha = E \end{cases}. \tag{70}$$

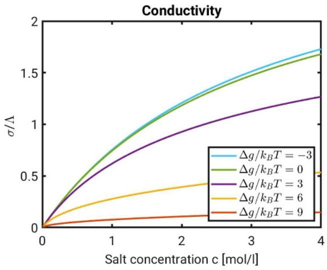

Fig. 5. Impact of dissociation energy Δg on the conductivity for an electrolyte without solvation ($\kappa = 0$), $\mathcal{D}_{0\pm} = \mathcal{D}_{E\pm} = \bar{\mathcal{D}}$ and $\mathcal{D}_{+-} = \mathcal{D}_{E0} = \bar{\mathcal{D}}/10$.

Inserting the diffusion fluxes (16) yields

$$\rho\big(\partial_t \omega_e + \boldsymbol{v}\cdot\nabla\omega_e\big) = \operatorname{div}\big(\rho D\,\nabla\omega_e\big) - \left(\sum_{\alpha\in\{+,-,E\}} \frac{\delta_\alpha m_\alpha}{z_\alpha e_0}\nabla t_\alpha\right)\boldsymbol{J}^{\mathrm{F}}, \tag{71}$$

where the salt diffusion coefficient D is defined as

$$D = \frac{1}{\rho}\sum_{\alpha,\beta\in\{+,-,E\}} \delta_\alpha \left(\frac{M_{\alpha\beta}}{T} - \sigma\frac{m_\alpha}{z_\alpha e_0}\frac{m_\beta}{z_\beta e_0} t_\alpha t_\beta\right)\frac{d(\mu_\beta - \mu_0)}{d\omega_e}. \tag{72}$$

As before the balance equation (71) reduces to the simple diffusion equation (61) for the salt concentration, given that the mass density ρ is almost constant, the barycentric velocity vanishes and no electric current flows.

With the definition (15) in terms of the mobility matrix $M_{\alpha\beta}$ in mind, it might seem at first glance, that σ and t_+ are the same for complete and incomplete dissociation. Similarly, it might seem that (72) just adds some terms to (60). However, due to the rather complex relation between the Maxwell–Stefan coefficients and the mobility matrix according to (33) and (29), the newly introduced coefficients $\mathcal{D}_{E+}$, $\mathcal{D}_{E-}$ and $\mathcal{D}_{E0}$ also contribute to the mobilities $M_{\alpha\beta}$ for $\alpha,\beta \in \{+,-\}$. Therefore, the explicit representations (65) are not valid in the context of incomplete dissociation and the derivation of such explicit relations for incomplete dissociation does not appear promising. In the following parameter study, we thus take the Maxwell–Stefan diffusivities to compute $B_{\alpha\beta}$ according to (33) and (35) and then determine the mobility matrix $M_{\alpha\beta}$ by numerical inversion of the matrix with coefficients $B_{\alpha\beta}$.

Impact of dissociation energy Δg. The dissociation energy Δg controls at given salt concentration c the amount of ions in the solution, i.e. the dissociation degree n_+/c, cf. Figure 1. Larger values of the dissociation energy thus decrease the conductivity of the electrolyte, see Figure 5 for electrolytes without solvation. In contrast to complete dissociation, the salt diffusion coefficient D can now change significantly over the range of salt concentrations, depending on the diffusivity coefficients $\mathcal{D}_{E+}$, $\mathcal{D}_{E-}$ and $\mathcal{D}_{E0}$, as studied below in more detail. Deviations from the complete dissociation case with a constant value of D get stronger as Δg increases. Similarly, the diffusivity coefficients $\mathcal{D}_{E+}$, $\mathcal{D}_{E-}$ and $\mathcal{D}_{E0}$ also have influence on the transference number of an incompletely dissociated electrolyte at higher salt concentrations, as studied below.

In the following, we keep the dissociation energy fixed at $\Delta g = 3k_BT$.

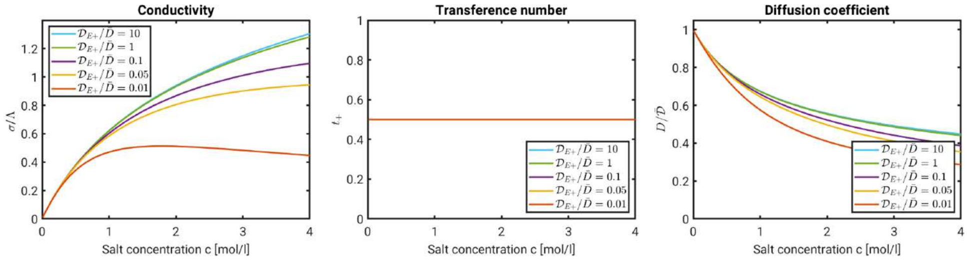

Fig. 6. Impact of $\mathcal{D}_{E\pm}$ on the transport parameters when $\mathcal{D}_{E+} = \mathcal{D}_{E-}$. Plots for conductivity (left), transference number (middle) and salt diffusion coefficient (right). The remaining parameters are $\kappa = 0$, $\Delta g = 3k_BT$, $\mathcal{D}_{0\pm} = \bar{\mathcal{D}}$ and $\mathcal{D}_{E0} = \mathcal{D}_{+-} = \bar{\mathcal{D}}/10$.

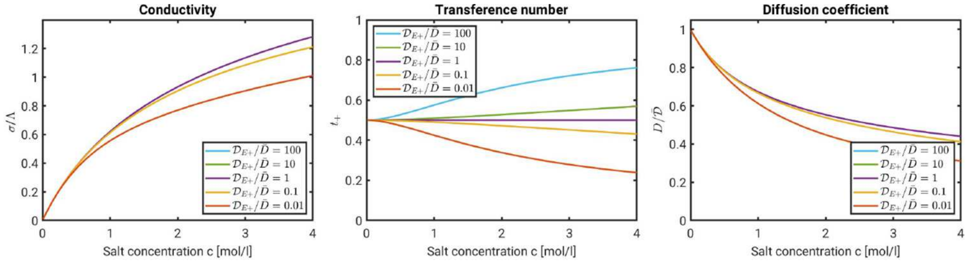

Fig. 7. Impact of $\mathcal{D}_{E\pm}$ on the transport parameters when $\mathcal{D}_{E+}\mathcal{D}_{E-} = \bar{\mathcal{D}}^2$. Plots for conductivity (left), transference number (middle) and salt diffusion coefficient (right). The remaining parameters are $\kappa = 0$, $\Delta g = 3k_BT$, $\mathcal{D}_{0\pm} = \bar{\mathcal{D}}$ and $\mathcal{D}_{E0} = \mathcal{D}_{+-} = \bar{\mathcal{D}}/10$.

Impact of the salt-solvent and salt-ion diffusion coefficients. The salt-ion diffusivities have a strong impact on all three transport parameters, see Figures 6 and 7. In particular, they can change the qualitative behavior of the conductivity curves. If both salt-ion diffusivities are small, $\mathcal{D}_{E+} = \mathcal{D}_{E-} < \bar{\mathcal{D}}$, the conductivity is lower than for complete dissociation and can even become non-monotone function of the salt concentration.

In contrast to the complete dissociation, the transfer number t_+ does in general not approach 1/2 for high salt concentrations. Even more, if $\mathcal{D}_{0+} = \mathcal{D}_{0-}$ then t_+ deviates from 1/2 if the salt-ion diffusivities $\mathcal{D}_{E+}$ and $\mathcal{D}_{E-}$ differ from each other, see Figure 7.

The salt-ion diffusivities also influence the salt diffusion coefficient, where the reduction of D is more pronounced $\mathcal{D}_{E+}, \mathcal{D}_{E-} < \bar{\mathcal{D}}$ than the increase of D for $\mathcal{D}_{E+}, \mathcal{D}_{E-} > \bar{\mathcal{D}}$, see Figure 6. The salt-solvent diffusivity $\mathcal{D}_{E0}$ expectable only influences the salt diffusion coefficient, as illustrated in Figure 8 for varying salt concentration. We observe that D can be monotone increasing if $\mathcal{D}_{E0}$ is comparable or larger than $\bar{\mathcal{D}}$. Conductivity and transference number are not significantly affected by variation of $\mathcal{D}_{E0}$.

Impact of solvation number κ. We choose small values for the salt-ion and salt-solvent diffusivities, i.e. $\mathcal{D}_{E\pm} = \mathcal{D}_{E0} = \bar{\mathcal{D}}/10$ and study in Figure 9 the variation of the transport parameters in dependence of the solvation number κ. Increasing the solvation number amplifies the influence of $\mathcal{D}_{E\pm}$ and $\mathcal{D}_{E0}$ and thus decreases the conductivity and the salt diffusion coefficient. Most notably, all conductivity curves are monotone, in contrast to Figure 4 for complete dissociation.

Taking a fixed value $\kappa = 4$ for the solvation number, we study the impact of the salt-ion and salt-solvent diffusivities. Comparison of Figure 7 left and Figure 10

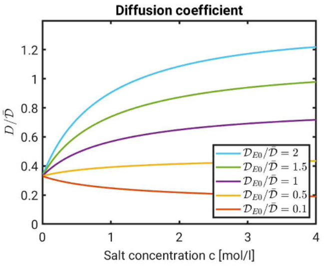

Fig. 8. Impact of $\mathcal{D}_{E0}$ on the salt diffusion coefficient D. The remaining parameters are $\kappa = 0$, $\Delta g = 3k_BT$ and $\mathcal{D}_{0-} = \mathcal{D}_{0+}/10$, $\mathcal{D}_{E\pm} = \bar{\mathcal{D}}$ and $\mathcal{D}_{+-} = \bar{\mathcal{D}}/10$.

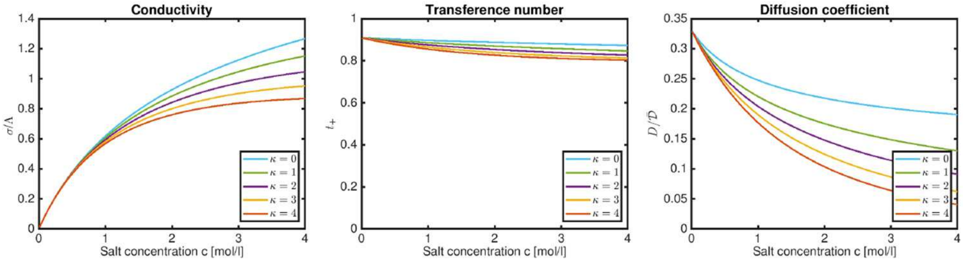

Fig. 9. Impact of the solvation number κ on conductivity (left), transference number (middle) and salt diffusion coefficient (right) for $\mathcal{D}_{0-} = \mathcal{D}_{0+}/10$ and $\mathcal{D}_{+-} = \mathcal{D}_{E\pm} = \mathcal{D}_{E0} = \bar{\mathcal{D}}/10$. Dissociation energy is $\Delta g = 3k_BT$.

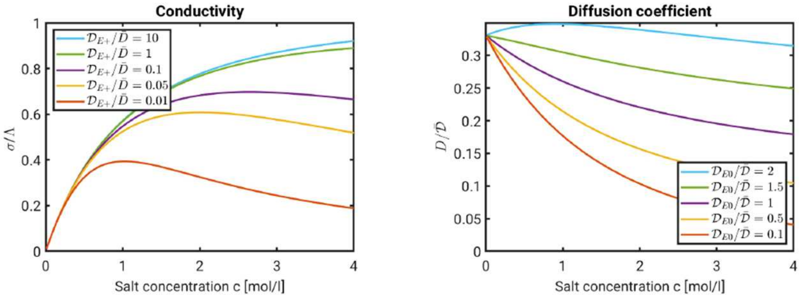

Fig. 10. Impact of salt-ion and salt-solvent diffusivities for fixed solvation number $\kappa = 4$. Left: dependence of the conductivity on variation of $\mathcal{D}_{E+}$ with the remaining parameters as in Figure 6. Right: salt diffusion coefficient when varying $\mathcal{D}_{E0}$ and the remaining parameters as in Figure 8.

left shows that ion solvation reduces the conductivity σ and non-monotonicity can already be observed for larger values of $\mathcal{D}_{E+}$. Compared to Figure 8, the ion solvation decreases the salt diffusion coefficient at higher salt concentrations see Figure 10 right. As a consequence, all curves of D are monotone decreasing for larger salt concentrations and we only observe an initial increasing behavior of the salt diffusion coefficient in the non-monotone curve for $\mathcal{D}_{E0} = 2\bar{\mathcal{D}}$.

6 Discussion and conclusion

The transport parameters of electrolytes combine in a rather complex way different effects which are related to both the free energy and to the kinetic coefficients. These two ingredients are modeled with theories of different origin and thus one must guarantee that the transport parameters combine the two theories in a consistent way.

Thermodynamic consistency. At several places in the literature, the thermodynamic consistency of the concentrated solution transport theory is discussed. A particular issue in the context of thermodynamic consistency is the admissibility of negative transference numbers. Based on experimental measurements, negative cation transference numbers t_+ have been reported for several polymer electrolytes [5,17], but also for liquid electrolytes containing some zinc-halides [23].

To guarantee a non-negative entropy production the authors of [17] impose on the Maxwell–Stefan diffusivities $\mathcal{D}_{\alpha\beta}$ for electrolytes with a complete dissociated salt the constraints (written in the notation of the current paper)

$$\text{(p. 1866 of [17]):} \qquad \frac{n_\alpha}{\mathcal{D}_{\alpha\gamma}} + \frac{n_\beta}{\mathcal{D}_{\alpha\beta}} \geq 0, \qquad \frac{n_\gamma}{n_\alpha \mathcal{D}_{\gamma\beta} + n_\beta \mathcal{D}_{\alpha\gamma}} + \frac{1}{\mathcal{D}_{\alpha\beta}} \geq 0, \tag{73}$$

and conclude (p. 1866 of [17]): “these two conditions place no limit on the sign or magnitude of the transference number”. In [16], the condition required for thermodynamic consistency is formulated in our notation as

$$\text{(p. 650 of [16])} \qquad \widetilde{\tau}_{\alpha\beta} \qquad \text{is symmetric and positive semi-definite,} \tag{74}$$

where the definition of $\widetilde{\tau}_{\alpha\beta}$ is identical to (35). The authors conclude (p. 650 of [16]): “Be aware that ... this does not in principle restrict all the Maxwell–Stefan coefficients to be positive” and moreover (p. 655 of [16]): “the transference number t_-^0 (or t_+^0) can take any real value”.

However, as stated before in [1], (37) imposes on the coefficients $\widetilde{\tau}_{\alpha\beta}$ in addition to (74) also the condition

$$\widetilde{\tau}_{\alpha\beta} \leq 0 \quad \text{implying} \quad \mathcal{D}_{\alpha\beta} \geq 0 \quad \text{for} \quad \alpha \neq \beta. \tag{75}$$

in order to guarantee a non-negative entropy production. In the case of a binary electrolyte with completely dissociated salt this implies non-negativity of $t_+ \geq 0$, according to (65a). For dilute solutions we have due to (45),

$$\text{(dilute solution limit)} \qquad t_\alpha = \frac{(z_\alpha e_0)^2}{\sigma} \frac{n_\alpha \mathcal{D}_{0\alpha}}{k_B T} \geq 0 \qquad \text{for } \alpha = 0, \ldots, N. \tag{76}$$

This is in full agreement with the reported experimental results of [5,17,23] mentioned above, since for low salt concentrations the transference numbers are positive and only become negative for high salt concentration.

The occurrence of negative t_+ necessarily requires the application of more complex models for mixtures consisting of more than three constituents. For electrolyte mixtures containing a partially dissociated salt, we are not able to adjust the parameters in a way that a negative transference number would result. This does not guarantee the non-negativity of t_+ in general, although we see no reason to expect $t_+ < 0$ in this setting if $\mathcal{D}_{\alpha\beta} \geq 0$ for $\alpha \neq \beta$. If more complex mixtures containing more than two charged species are considered, negative transference number might appear at finite salt concentrations.

Transport parameters. The transport in an electrolyte resulting from dissociation of a single neutral salt into anions and cations in a neutral solvent is controlled by the three transport parameters conductivity σ, transference number t_+ and salt diffusion coefficient D. This holds independent of whether the salt dissociation is complete or incomplete. Maxwell–Stefan theory for a mixture of four constituents provides six independent diffusivity coefficients to determine these three transport parameters in dependence of the salt concentration. In the case of complete dissociation, only three constituents and three independent diffusivity coefficients remain and in this case they already uniquely determine the transport parameters over the full range of salt concentrations.

From the numerical study we draw the following conclusions:

- The conductivity strongly depends on the number of available ions in the electrolyte and the mean value $\bar{\mathcal{D}}$ of the ion–solvent diffusivities, but not on the ratio $\mathcal{D}_{0+}/\mathcal{D}_{0-}$. Therefore, we observe a monotone growth of the conductivity with respect to the salt concentration in a large parameter range. There are two exceptions: (i) in the case of complete dissociation, solvation causes for increasing salt concentration a strong decrease of the solvent number density, such that the impact of the ion–ion diffusivity $\mathcal{D}_{+-}$ becomes dominant. If $\mathcal{D}_{+-} \ll \bar{\mathcal{D}}$, then the conductivity becomes non-monotone with respect to salt concentration. (ii) For incomplete dissociation, low salt-ion diffusivities $\mathcal{D}_{E\pm} \ll \bar{\mathcal{D}}$ reduce the ion mobility and thereby can cause non-monotone conductivity with respect to the salt concentration.

  In case of non-monotone conductivity, the maximum of the conductivity is attained at lower salt concentrations when increasing the solvation number or decreasing the salt-ion diffusivities.

- The transference number t_+ at low salt concentrations is determined by the ratio $\mathcal{D}_{0+}/\mathcal{D}_{0-}$. For complete dissociation t_+ always tends to $1/2$ for large salt concentrations, whereas for incomplete dissociation, a transition to a different value can be observed, if the ratio $\mathcal{D}_{E+}/\mathcal{D}_{E-}$ is sufficiently different from $\mathcal{D}_{0+}/\mathcal{D}_{0-}$. Generally, ion solvation fosters these transition processes, most pronounced in the case of complete dissociation.

- For complete dissociation, the salt diffusion coefficient D depends only on $\mathcal{D}_{0+}$ and $\mathcal{D}_{0-}$ and is almost independent of the salt concentration. Thus, the thermodynamic factor is $\mathcal{F} \approx n_0/n$, independent of the salt concentration. Remarkably, this also holds for solvated ions with large solvation number where the considered salt concentration reaches close to the saturation limit. When the dissociation is incomplete, D is also influenced by $\mathcal{D}_{E\pm}$ and $\mathcal{D}_{E0}$, and this influence gets stronger, the more salt remains undissociated. Thus, when $\mathcal{D}_{E\pm}$ and $\mathcal{D}_{E0}$ are sufficiently different from $\bar{\mathcal{D}}$, the salt diffusion coefficient varies considerably with the salt concentration, often in a monotone way.

  For solvated ions, a non-monotone salt diffusion coefficient can be observed if the salt-solvent diffusion coefficient $\mathcal{D}_{E0} > \bar{\mathcal{D}} \approx \mathcal{D}_{E\pm}$.

Extensions of the continuum model. In order to limit the complexity of the model, we considered in this work only an isothermal electrostatic setting. However, the continuum model applied here is derived within a much more general framework of coupled bulk-surface electro-thermodynamics [12]. Therefore, an extended model containing the energy balance and the full set of Maxwell's equation can be thermodynamically consistently derived from the same framework. Moreover, the framework allows the continuum model applied here to be easily adapted to different electrolytes like solid and polymer electrolytes. Such an adaption only requires the derivation of suitable free energy models for solid or polymer electrolytes to replace the free energy model for liquid electrolytes defined in Section 3.1. Then, the impact on mechanical stresses within the crystal lattice in solids or the length of the polymer chains on the transport parameters can be studied.

The authors gratefully acknowledge support by the Einstein Foundation Berlin within the MATHEON Project CH11 "Sensing with Nanopores".

Author contribution statement

All authors contributed equally to the paper.

References

1. D. Bothe, W. Dreyer, Acta Mech. **226**, 1757 (2015)
2. A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications* (Wiley, New York, 2000)
3. A.M. Bizeray, D.A. Howey, C.W. Monroe, J. Electrochem. Soc. **163**, E223 (2016)
4. J.E. Dykstra, P.M. Biesheuvel, H.Bruning, A. Ter Heijne, Phys. Rev. E **90**, 013302 (2014)
5. M.M. Doeff, L. Edman, S.E. Sloop, J. Kerr, L.C. De Jonghe, J. Power Sources **89**, 227 (2000)
6. W. Dreyer, C. Guhlke, M. Landstorfer, Electrochem. Commun. **43**, 75 (2014)
7. W. Dreyer, C. Guhlke, M. Landstorfer, R. Müller, Eur. J. Appl. Math. **29**, 708 (2018)
8. S.R. de Groot, P. Mazur, *Non-Equilibrium Thermodynamics* (North Holland, Amsterdam, 1962)
9. W. Dreyer, C. Guhlke, R. Müller, Phys. Chem. Chem. Phys. **15**, 7075 (2013)
10. W. Dreyer, C. Guhlke, R. Müller, Phys. Chem. Chem. Phys. **17**, 27176 (2015)
11. W. Dreyer, C. Guhlke, R. Müller, Phys. Chem. Chem. Phys. **18**, 24966 (2016)
12. W. Dreyer, C. Guhlke, R. Müller, Entropy **20**, 939 (2018)
13. R. Datta, S.A. Vilekar, Chem. Eng. Sci. **65**, 5976 (2010)
14. M.S. Kilic, M.Z. Bazant, A. Ajdari, Phys. Rev. E **75**, 021502 (2007)
15. M. Landstorfer, C. Guhlke, W. Dreyer, Electrochim. Acta **201**, 187 (2016)
16. C.W. Monroe, C. Delacourt, Electrochim. Acta **114**, 649 (2013)
17. Y. Ma, M. Doyle, T.F. Fuller, M.M. Doeff, L.C. De Jonghe, J. Newman, J. Electrochem. Soc. **142**, 1859 (1995)
18. C.W. Monroe, Ionic mobility and diffusivity, in *Encyclopedia of Applied Electrochemistry*, edited by G. Kreysa, K. Ota, R.F. Savinell (Springer, New York, 2014), pp. 1125–1130
19. I. Müller, *Thermodynamics* (Pitman Publishing, London, 1985)
20. J. Newman, K.E. Thomas-Alyea, *Electrochemical Systems* (Wiley, Hoboken, NJ, 2004)
21. Y.S. Oren, P.M. Biesheuvel, Phys. Rev. Appl. **9**, 024034 (2018)
22. A.M. Ramos, Appl. Math. Model. **40**, 115 (2016)
23. R.H. Stokes, B.J. Levien, J. Am. Chem. Soc. **68**, 1852 (1946)
24. W.H. Smyrl, J. Newman, J. Phys. Chem. **72**, 4660 (1968)
25. G.L. Standart, R. Taylor, R. Krishna, Chem. Eng. Commun. **3**, 277 (1979)
26. M. Tedesco, H.V.M. Hamelers, P.M. Biesheuvel, J. Membrane Sci. **531**, 172 (2017)
27. R. Taylor, R. Krishna, in *Multicomponent Mass Transfer* (John Wiley & Sons, New York, 1993), Vol. 2
28. C. Truesdell, J. Chem. Phys. **37**, 2336 (1962)
29. G. Wedler, *Lehrbuch der Physikalischen Chemie* (Wiley-VCH, Weinheim, 2004)