

Resurrection of Hückel’s idea: decoupling ion-ion and ion-water terms in activity coefficients via the state-dependent dielectric constant

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Abstract

Although Hückel proposed the basic idea of using a concentration dependent dielectric constant, $\epsilon(c)$, to compute the activity coefficients of ions in electrolytes in 1925 (Hückel, Phys. Z. 26 (1925) 93–147.), a large amount of modeling studies appeared in the literature only after 2010 when we published our II+IW theory (Vincze et al., J. Chem. Phys. 133 (2010) 154507.) that splits the excess chemical potential into two terms corresponding to interactions between ions (II) and interactions between ions and water (IW). In this approach, the two terms are decoupled, which means that they can be computed independently with $\epsilon(c)$ being the only link between them. Here, we review our theory and other works based on Hückel’s suggestion by discussing several issues that are partly cornerstones of the theory, partly make it possible to put the theory into a larger context. These issues include the role of $\epsilon(c)$ and the ionic radii used in the II and IW term, the statistical mechanical methods to estimate the II term, the existence and interpretation of individual activities, phenomena associated with strong ionic correlations in multivalent electrolytes, and explicit-water models used in molecular dynamics simulations.

1. Introduction

In a 2010 paper [1] we proposed the II+IW theory in which the excess chemical potential of ions in an electrolyte is split into two terms as

$$\mu_i^{\text{EX}} = \mu_i^{\text{II}} + \mu_i^{\text{IW}}, \quad (1)$$

where the II term corresponds to ion-ion, while the IW term to ion-water (solvation) interactions. This work was followed by several other ones [2–6] describing temperature dependence, individual activity coefficients, and multivalent electrolytes.

The II term can be computed using various statistical mechanical theories (from the Debye-Hückel (DH) theory [7] to Monte Carlo (MC) simulations), while the IW term is straightforwardly estimated by Born’s theory of solvation [8]. The II+IW theory is based on the implicit-solvent framework of electrolytes, where the solvent (for simplicity, we talk about water, but it can be anything) is a dielectric continuum characterized by a concentration-dependent dielectric constant, $\epsilon(c)$. The link between the II and IW terms is $\epsilon(c)$. The motivation for developing the theory was to explain the non-monotonic concentration dependence of the mean activity coefficient of electrolytes.

Although we were not aware of it at the time (2010), the basic idea of the theory (the concentration dependent dielectric constant and splitting the excess chemical potential into ionic and solvation terms) was already suggested by Hückel in 1925 [9] and by Teitler and Ginsburg [10] in 1956.

Until 2010, the the concentration-dependent dielectric constant was used either as an adjustable parameter [11–13] or as an experimental input [14–16], but the IW term was ignored in these studies. Ionic radii were adjusted instead to take solvation into account. In 2010, we found only two papers in the literature, where the IW term was included. [17, 18]

Since 2015, Hückel’s idea has been enjoying a renaissance resulting in a landslide of papers. Liu and Eisenberg developed the Poisson-Fermi theory using a concentration-dependent dielectric constant to describe changes in the hydration shell. [19–21] Shilov and Lyashchenko proposed the Extended DH theory. [22–31] Kontogeorgis and several coworkers applied the idea in a series of papers using various methods to account for the II term. [32–41] The concentration dependent dielectric constant and the Born-term was taken into account in many studies focusing on various phenomena. [42–59]

We sincerely hope that we did not miss any paper from the above list. Discussing them one by

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one, however, is beyond the scope of this work. Instead, after presenting our theory in section 2, we provide a detailed analysis of a number of issues where those papers will surface. These issues that we feel are important in relation to Hückel’s idea and the II+IW theory include the role of $\epsilon(c)$ and the decoupling of the II and IW terms (apart from $\epsilon(c)$ linking them, sections 3.1 and 3.2), the choice of the Born (section 3.3) and the ionic (section 3.4) radii, the necessity of fitting (section 3.5), the statistical mechanical methods to estimate the II term (section 3.6), the existence and interpretation of individual activities (section 3.7), multivalent electrolytes with strong ionic correlations (section 3.8), and explicit-water models used in molecular dynamics (MD) simulations (section 3.10).

Our purpose with the discussion of these issues and with the whole paper is to promote the core idea of the theory as it was suggested by Hückel: the concentration dependent dielectric constant and the balance of the II and IW terms that follows from it. We hope this idea will find its way into more developed theories and equations of state in the future. We are trying to catalyze this process and by describing the merits of this approach.

In our view, the need for the II+IW terms for which we advocate stems from two inescapable facts: the experimental result that dielectric constant changes with ion concentration and that not including them in a theory excludes known and important ion configurations, especially at high concentrations.

2. The II+IW theory in a nutshell

2.1. Activity coefficients

The individual activity coefficient, γ_i , in an electrolyte solution describes the deviation from ideality through the excess chemical potential

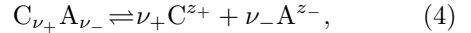
$$\mu_i^{\text{EX}} = kT \ln \gamma_i \quad (2)$$

defined by

$$\mu_i = \mu_i^0 + kT \ln c_i + \mu_i^{\text{EX}}, \quad (3)$$

where μ_i is the chemical potential of species i , c_i is its concentration, μ_i^0 is a reference chemical potential independent of the concentration, k is Boltzmann’s constant, and T is the temperature. The reference state for electrolytes is the infinite dilution case, where μ_i^0 contains the interaction of an ion with water, while for the excess part we have $\lim_{c \rightarrow 0} \mu_i^{\text{EX}} = 0$ and $\lim_{c \rightarrow 0} \gamma_i = 1$. [60]

For pure electrolytes, the salt concentration is defined as $c = c_+/\nu_+ = c_-/\nu_-$ with ν_+ and ν_- being the stoichiometric coefficients of the cation, C, and the anion, A, in a simple electrolyte with the stoichiometry



where z_+ and z_- are the valences of the ions. The mean activity coefficient is defined as

$$\gamma_{\pm} = \gamma_+^{\nu_+/\nu} \gamma_-^{\nu_-/\nu}, \quad (5)$$

where $\nu = \nu_+ + \nu_-$. Accordingly, the mean excess chemical potential is computed as

$$\mu_{\pm}^{\text{EX}} = \frac{\nu_+}{\nu} \mu_+^{\text{EX}} + \frac{\nu_-}{\nu} \mu_-^{\text{EX}}. \quad (6)$$

The mean quantities, γ_{\pm} and μ_{\pm}^{EX} , can be measured accurately [61–63].

2.2. The ion-ion term

The II term corresponds to the interactions of ions in a dielectric continuum of dielectric constant $\epsilon(c)$. It can be calculated on the basis of various models in the framework of the implicit solvent approach. The common ground is that only ions are modeled explicitly, while the solvent is represented as an implicit continuum with a dielectric constant $\epsilon(c, T)$.

While continuum theories describe distributions of ions with functions obeying, at a minimum, the Boltzmann probability distribution and Poisson’s equation, more developed statistical mechanical theories (see section 3.6) use explicit molecular models. The most widely spread explicit model for the ions used in these theories is the Primitive Model (PM) of electrolytes, where the pair-potential is given as

$$u_{ij}^{\text{PM}}(r) = \begin{cases} \infty & \text{for } r < R_i + R_j \\ \frac{z_i z_j e^2}{4\pi\epsilon_0\epsilon(c, T)r} & \text{for } r \geq R_i + R_j. \end{cases} \quad (7)$$

Here, R_i is the radius of ionic species i , ϵ_0 is the permittivity of vacuum, and r is the distance between the ions.

We used this model to compute the II term using Grand Canonical Monte Carlo (GCMC) simulations. The advantage of computer simulations is that they compute the many-particle correlations exactly for a given model. While system size dependence and inadequate sampling limit accuracy in simulations, theories contain “built-in” approximations that can be quite serious when strong correlations (see section 3.8) are present in the system.

2.3. The ion-water term

The IW term corresponds to the interaction of an ion with the surrounding dielectric continuum of dielectric constant $\epsilon(c)$. It can be estimated from Born's theory of solvation [8] via the following parameterization. The solvation free energy, ΔG_i^s , is the experimentally attainable quantity. It is the free energy difference between the ion being in the solution and in a reference state (vacuum). [64] Born's theory estimates it with the electrostatic energy change of the insertion of a spherical bubble of radius $R_i^B(T)$ with a charge $z_i e$ in its center in the continuum of dielectric constant $\epsilon_w(T)$:

$$\Delta G_i^s(c \rightarrow 0, T) = \frac{z_i^2 e^2}{8\pi\epsilon_0 R_i^B(T)} \left(\frac{1}{\epsilon_w(T)} - 1 \right), \quad (8)$$

where $\epsilon_w(T)$ is the dielectric constant of water (the $c \rightarrow 0$ limit) at temperature T ($\epsilon_w = 78.37$ for $T = 298.15$ K). It is important to note that the radius $R_i^B(T)$ (the Born radius) does not have to be the same as R_i used in the calculation of the II terms (see section 3.1). The Born radius is not a real physical radius, but an effective parameter obtained from the approximate Born theory, Eq. 8 (see section 3.3). Practically, the Born radius is defined by the Born equation so that ΔG_i^s matches experimental data.

If concentration is large, we define a corresponding solvation free energy as

$$\Delta G_i^s(c, T) = \frac{z_i^2 e^2}{8\pi\epsilon_0 R_i^B(T)} \left(\frac{1}{\epsilon(c, T)} - 1 \right). \quad (9)$$

This term describes the interaction of an ion with the surrounding water by ignoring other ions. It is the concentration-dependent dielectric constant, $\epsilon(c, T)$, on the right-hand side of the equation that carries any information about the presence of other ions (see section 3.2). That the IW interactions can be characterized by the dielectric constant of the solution has been debated by Simonin recently. [48, 65]

Because the IW term of μ_i^{EX} describes the interaction of the inserted ion "only" with water, we identify μ_i^{IW} with the solvation free energy. In particular, because the reference state is the infinitely diluted solution, we write that

$$\mu_i^{\text{IW}}(c, T) = \Delta G_i^s(c, T) - \Delta G_i^s(c \rightarrow 0, T). \quad (10)$$

Substituting Eqs. 9 and 8 into Eq. 10, we obtain that

$$\mu_i^{\text{IW}}(c, T) = \frac{z_i^2 e^2}{8\pi\epsilon_0 R_i^B(T)} \left(\frac{1}{\epsilon(c, T)} - \frac{1}{\epsilon_w(T)} \right). \quad (11)$$

Table 1: Experimental parameters of ions: the valence, z_i , the Pauling radius [67], R_i , the solvation Gibbs free energy, ΔG_i^s [63, 68], and the Born radius, R_i^B (computed from ΔG_i^s on the basis of Eq. 8 with $\epsilon_w = 78.37$), for $T = 298.15$ K.

Ion	z_i	$R_i/\text{\AA}$	$\Delta G_i^s/\text{kJmol}^{-1}$	$R_i^B/\text{\AA}$
Na ⁺	1	0.95	-424	1.62
Ca ²⁺	2	0.99	-1608	1.71
La ³⁺	3	1.05	-3145	1.96
Cl ⁻	-1	1.81	-304	2.26

Because the Born radius is a constant source of misunderstanding (section 3.3), we prefer the expression that contains the solvation free energy rather than the Born radius:

$$\mu_i^{\text{IW}}(c, T) = \Delta G_i^s(T) \frac{\epsilon(c, T) - \epsilon_w(T)}{\epsilon(c, T)(\epsilon_w(T) - 1)}. \quad (12)$$

This equation was obtained from expressing $R_i^B(T)$ from Eq. 8 and substituting it into Eq. 11. This expression contains only experimentally measurable parameters: $\Delta G_i^s(T)$, $\epsilon(c, T)$, and $\epsilon_w(T)$. Note that $\mu_i^{\text{IW}}(c, T) > 0$ if $\epsilon(c, T) < \epsilon_w(T)$ and $\Delta G_i^s(T) < 0$.

Eq. 12 was first published by Nonner et al. to estimate the change in the hydration part of the excess chemical potential of an ion in going from the bath to a different dielectric environment, the selectivity filter of an ion channel. [66]

2.4. Representative results

To illustrate how the theory works, here we show results for NaCl, CaCl₂, and LaCl₃. [1, 5, 6] Model parameters (experimental values) are collected in Table 1, while the concentration dependent dielectric constant is shown in Fig. 1.

The mean activity coefficients are shown in Fig. 2A in comparison with experimental data. The agreement is qualitative, but the non-monotonic behavior is reproduced without any adjustable parameter.

The II and IW components are seen in panels (B)-(D) for NaCl, CaCl₂, and LaCl₃, respectively. Both the II and IW terms increase in magnitude (the IW term is positive, while the II term is negative) as c increases, but they increase in a different manner so their sum produces the non-monotonic behavior of the excess chemical potential.

3. Elements of the II+IW theory in a deeper context

In the following, we analyze a series of issues that we believe relevant for Hückel's original idea and theories based on it, such as the II+IW approach.

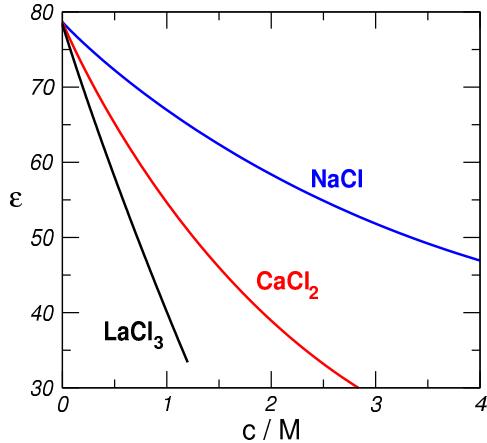


Figure 1: The dielectric constant as a function of concentration for NaCl, CaCl₂, and LaCl₃ as obtained from measurements. The curves are fits to experimental data given by $\epsilon(c)=78.37 - 15.45 c + 3.76 c^{3/2}$ for NaCl [69], $\epsilon(c)=78.37 - 34 c + 10 c^{3/2}$ for CaCl₂ [70, 71], and $\epsilon(c)=78.37 - 46.48 c + 8.21 c^{3/2}$ for LaCl₃ [62, 72].

3.1. Decoupling of the II+IW terms

This is a basic approximation of the theory. Fundamentally, parts of the chemical potential corresponding to II and IW interactions cannot be decoupled rigorously. Take, for example, the Widom test particle method [79] to compute the excess chemical potential of species A in a mixture of $A + B$.

In this method, test particles of species A are inserted in the simulation cell and the interactions with other particles of species A and B are computed as

$$\Delta U_{AA} = \sum_{i=1}^{N_A} u_i^{AA} \quad (13)$$

and

$$\Delta U_{AB} = \sum_{i=1}^{N_B} u_i^{AB}, \quad (14)$$

respectively, where u_i^{AA} is the pair-interaction of the test particle with the i th “real” particle of species A in the simulation cell, u_i^{AB} is the pair-interaction of the test particle with the i th “real” particle of species B in the simulation cell, while N_A and N_B are the numbers of “real” particles in the simulation cell of species A and B , respectively (pair-wise additivity is assumed). The test particles are not left in the simulation cell after insertion; that is why they are also called “ghost” particles and distinguished from the “real” particles. Their sole purpose is sampling.

This insertion is performed many times during the simulation and the excess chemical potential

is computed as

$$\mu_A^{\text{EX}} = -kT \ln \left\langle \exp \left(-\frac{\Delta U}{kT} \right) \right\rangle, \quad (15)$$

where

$$\Delta U = \Delta U^{AA} + \Delta U^{AB} \quad (16)$$

is the total potential energy of an inserted particle, and the brackets denote ensemble average over the insertions of the test particles.

Decoupling the energy into AA and AB terms is natural (Eq. 16), but the decoupling of the excess chemical potential into AA and AB terms is necessarily arbitrary because

$$\ln \left\langle \exp \left(-\frac{\Delta U}{kT} \right) \right\rangle \neq \ln \left\langle \exp \left(-\frac{\Delta U^{AA}}{kT} \right) \right\rangle + \ln \left\langle \exp \left(-\frac{\Delta U^{AB}}{kT} \right) \right\rangle. \quad (17)$$

MD simulations generally just report the total excess chemical potential, computed from the Widom method or thermodynamic integration, exactly because of this arbitrariness.

Decomposition of the chemical potential into various terms, however, can be useful because it can shed light on interesting physical mechanisms, even if the decomposition is arbitrary. Gillespie, for example, suggested a decomposition into hard sphere and electrostatic terms for the PM model using Density Functional Theory (DFT) to describe ionic competition in ion channels [80] and at electrified interfaces [81]. The electrostatic term was further broken into a mean-field and a so called “screening” term, where the mean-field term describes the interaction of the ion with the mean electrostatic potential, while the “screening” term describes electrostatic correlations beyond mean field. While defining these terms is straightforward in DFT, it is less so in a computer simulation. Therefore, we developed a method for the decomposition in GCMC simulations also including terms describing polarization (interact with induced charges). [82, 83]

In the II+IW theory, we admittedly decouple the excess chemical potential into II and IW terms in an arbitrary way that, nevertheless, has a well-established physical basis. Statistical mechanical theories and equations of state [18, 39, 40, 54, 59, 84–90] break the chemical potential into various terms, but the arbitrary manner of this decomposition is rarely emphasized.

The basis of decoupling in our model is that (1) water is implicit and that (2) the dielectric constant is state dependent. (1) The implicit water treatment is already such a serious approximation

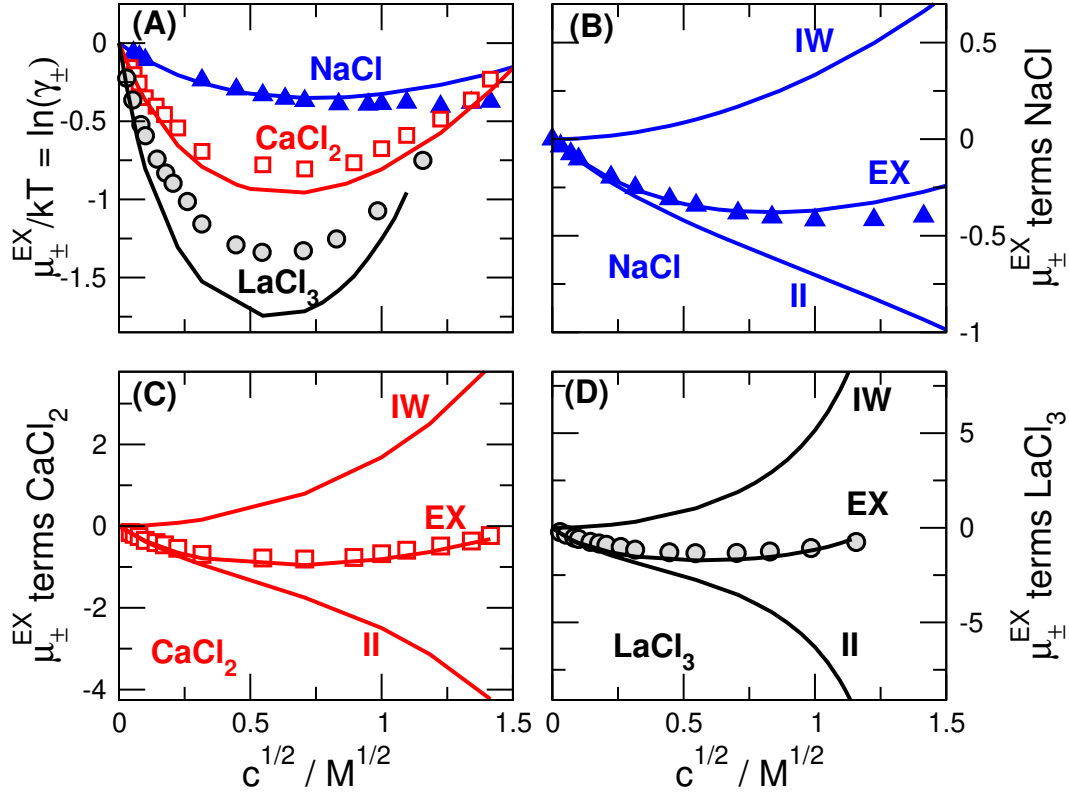


Figure 2: (A) The mean activity coefficient as a function of concentration for NaCl, CaCl₂, and LaCl₃ as obtained from experiments (symbols) and the II+IW theory (lines). The experimental data are from Wilczek-Vera et al. [73] for NaCl, from several works [73–76] for CaCl₂, and from Hurlen [77] and Fang et al. [78] for LaCl₃. (B)–(D) Mean excess chemical potentials and the II and IW terms for NaCl (B), CaCl₂ (C), and LaCl₃ (D), see Eq. 2. The II terms are computed from GCMC simulation for the PM given in Eq. 7, while the IW terms are computed from Eq. 12. The parameters are found in Table 1 and in the caption of Fig. 1. The results are from Refs. [1, 3, 6]

that arbitrariness in the decomposition of the II and IW terms is not a problem as soon as we are explicit about it. (2) The c dependent dielectric constant is practically the heart of the decoupling; this is what appears in both terms characterizing the change in the aqueous environment of the ion: as concentration increases, water is less able to solvate the ion and it is less able to screen the Coulomb interactions between the ions.

3.2. Concentration dependent dielectric constant

The dielectric constant characterizes the ability of water molecules to screen the electric field including the electric field produced by an ion. The dielectric constant of an electrolyte solution decreases with increasing concentration because ions orient the water molecules. This decreases their ability to adjust their orientation in the solvation shell of an ion, and thus, the ability of water molecules to screen the charge of this ion.

The decreased ability of water to screen the ionic charges appears in both the II and IW terms. The Coulomb interaction between two ions becomes less screened (see $\epsilon(c)$ in the denominator

of Eq. 7), so the II term becomes more negative. The ions become less effectively solvated so the solvation free energy becomes larger than in the $c \rightarrow 0$ limit (see Eq. 11), so the IW term becomes more positive. In Mean Spherical Approximation (MSA) studies in the 1990s [11–16] the IW term was ignored. Solvation was taken into account by an increased “solvated ionic radius” in these papers, an issue that we will discuss in section 3.3.

Before 2010, the IW term was used by two groups to our best knowledge. Abbas et al. [17] used the Born theory to estimate the IW term, but they used the same value for the ionic radius in the ionic interactions in the II term (Eq. 7) and for the Born radius in the IW term (Eq. 11). This unnecessary assumption rendered their approach to fail, because using smaller radius the IW term was overestimated, while using larger radius the II term was underestimated (in magnitude). So they seemingly left possibility of decoupling the II and IW terms unexploited.

The two radii were also the same in the paper Shilov and Lyashchenko [22] in which they

suggested an extension of the DH theory in the II+IW framework. In a comment to their paper [4], we drew the community’s attention to the fact that these radii do not have to be the same. The distinction between the two radii, however, was made in the paper of Inchekel *et al.* [18] who used the Born term among several other terms in an equation of state.

All in our papers [1–6], we used experimental data for $\epsilon(c)$ reported by various authors [62, 69, 70, 72, 91–98]. We realized that the data are scarce due the difficult measurement methods. The data of Buchner *et al.* [69] from 1999, for example, differ from the data of Barthel *et al.* [70, 71] from the 1970s, because they used lower frequencies in their impedance measurements (200 MHz as opposed to 1 GHz). The measurement frequency considerably influences the extrapolation to zero frequency for the static dielectric constant.

The alternative to experimental data is using empirical and/or statistical mechanical theory to estimate the dielectric constant. [49, 84, 85, 99–112]

Note that several authors used terms containing the $\partial\epsilon/\partial c$ derivative in their treatment [12, 13, 16–18, 33–36, 41], while those terms were absent in other works. We do not use these terms in our theory in neither the IW nor the II terms. The IW term measures the energy cost of moving the ion from an favorable (good screening) dielectric environment into a less favorable (worse screening) dielectric environment. We ignore the presence of other ions during this process. In the calculation of the II term, we use the PM that corresponds to a Hamiltonian in which ϵ is a constant parameter depending on the thermodynamic state. In the GCMC simulation, we measure the free energetic consequences of density fluctuations, namely, inserting/deleting ions *locally*. We think of the excess chemical potential as a measure of the system’s response to a local disturbance, the insertion of a particle (see Widom’s test particle method, Eq.15). The insertion of an ion into a large system (see thermodynamic limit, Eq. 18), therefore, does not change the dielectric constant of the system.

Inserting an ion, however, can change the dielectric constant *locally*. This is, however, beyond the scope of our simple theory.

3.3. The problem of the solvated ionic radius

Agreement with experiment was possible in many theoretical works using a fixed dielectric constant (ϵ_w) only by increasing ionic radii in the II term above Pauling radii [67]. These works include extensions of the DH theory [17, 113–115],

MSA [11–16, 116–118], and simulation [17, 113]. The increased radius was interpreted as a “solvated” ionic radius of the ion that encloses not only the ion itself but also a tightly bound hydration shell of water molecules around the ion. The purpose of this model was to take solvation effects into account in the implicit water framework. Since the dielectric constant was independent of concentration, there was no other way in the framework of the model to include solvation.

We believe that the idea of the “solvated radius” is a concept that mislead modeling efforts for years. The reason that an increased ion size was able to reproduce the upswing part of the $\gamma_{\pm}(c)$ curve at high concentrations is that the larger “solvated” radius produced a larger hard sphere (HS) contribution in the II term. This is an excluded volume term that is positive, so it compensates for the more negative electrostatic term that appears at large concentrations because cations and anions are closer to each other on average.

We reasoned, however, that important configurations corresponding to cations and anions in contact are excluded from the statistical sample with the artificial concept of the “solvated radius”. Those configurations are extremely important at large concentrations close to the saturation limit when ions tend to associate. Artificially excluding these states leads to a distorted physical picture behind the competition leading to the non-monotonic behavior of the activity coefficient. The correct picture, in our view, is that advocated by Hückel: the competition between the II and IW terms produces the upswing.

It is hard to retrieve the historical origin of the concept of the solvated radius, but we can make some educated guesses. First, it might have been motivated by the hydrodynamic (or Stokes) radius of ions. It was known that the electrical conductance data in electrolytes could be reproduced with the Stokes-Einstein equation by assigning hydrodynamic radii to the ions that tune the frictional force (Stokes law) exerted on the migrating ions in the solvent. The hydrodynamic radius is larger than the Pauling radius, and it increases as the size of ions decreases. This finding can be interpreted by assuming that the hydration shell is more tightly bound to the smaller ions than to the larger ions.

The direct generalization of this idea to the issue of the activity coefficient is problematic because electrical conductance experiments are about the interaction of a diffusing ion with its surrounding medium, while the activity coefficient is an equilibrium quantity that depends delicately not only on interactions between ions and

water molecules, but also between two ions, a cation and an anion, most importantly. The non-monotonic behavior is produced by the balance of all these interactions. The concentration dependent dielectric constant proved to be a parameter that efficiently tuned these interactions as modeled by the II and IW terms in a simplified way.

The other historical reason behind the concept of the “solvated radius” might be the seminal papers of Torrie and Valleau (TV) who first used MC simulations to study the electrical double layer in the framework of the PM. [119–125] In those works, they consequently used the value $d=4.25$ Å for both cations and anions without any explanation for the choice of this number. In our 2002 paper [126] we guessed that “The value $d=4.25$ Å that was used by TV is somewhat large. Presumably, this value was chosen to be representative of a solvated ion.” In any case, that particular number somehow stuck in the practice of the modeling community.

When we started to work on ion selectivity in ion channels, we realized that experimental data can be interpreted only if we use Pauling radii. [127–135] When interactions of ions with surfaces, pores, structural groups, etc. are behind the studied phenomena (instead of the interaction of the ion with solvent), the “solvated radius” is no longer a useful concept: ions are supposed to approach those structural groups to make contact and bind to them physically.

3.4. The choice of ionic radius in the II term

If we accept that solvation is taken into account with the IW term associated with the concentration-dependent dielectric constant instead of an increased ionic radius in the II term and that the two terms (II and IW) can be computed independently (apart from $\epsilon(c)$ linking them together), we have some freedom to choose the values for the ionic radii, R_i , in the II term. Basically, (1) we can use experimentally motivated values, or (2) we can make them adjustable parameters.

Because our declared intention was not to use adjustable parameters in our calculations, we chose the first route and used the Pauling radii [67] for R_i . For NaCl electrolyte, however, we examined the consequences of other choices as well. [3] We applied the Shannon-Prewitt radii [136] and obtained results for γ_{\pm} very similar to those obtained with the Pauling radii. The explanation is that while the Shannon-Prewitt radius of Na^+ is larger than the Pauling radius (1.16 Å vs. 0.95 Å) the opposite is true for Cl^- (1.67 Å vs. 1.81 Å), the $\text{Na}^+\text{-Cl}^-$ contact distance (or, distance of closest approach,

DCA) is similar in the two cases as soon as the Lorentz-Berthelot (LB) mixing rules are assumed: $d_{+-}=R_+ + R_-=2.83$ vs. 2.76 Å.

During statistical sampling of the configurations, the low-energy (important) configurations are those when a cation and an anion are close to each other. The DCA of the cation and anion, therefore, is a parameter that is more important than the ionic radii themselves especially at large concentration (low $\epsilon(c)$) when the Coulomb interactions at contact are strong. Note that in the DH theory a distance parameter similar in meaning to d_{+-} is used.

The LB mixing rules, however, do not have to be applied necessarily, so that $d_{+-}\neq(d_+ + d_-)/2$. This is a basic assumption of the “smaller-ion shell” (SiS) theory of Fraenkel [114], for example. This is not surprising because the hydration shell may remain intact if the like-charged ions approach one another, while unlike-charged ions can dislodge the water molecules from their places so that the ions can get into contact. This is well demonstrated by radial distribution functions obtained from explicit-water MD simulations. [137–144]. DCAs can be deduced from the r distance where the first peak declines to zero. For aqueous NaCl, the following values have been deduced: $d_{++}=3$ Å, $d_{--}=4$ Å, and $d_{+-}=2.5$ Å. The unlike DCA is smaller than those from the LB mixing rule, so the II term is more negative. The calculations for γ_{\pm} using these DCA values are closer to experiments than those using the Pauling or Shannon-Prewitt values with LB mixing rule (see Fig. 4 of Ref. [3]).

The unlike DCA, d_{+-} , therefore, offers itself as an adjustable parameter whose value is not as physically well-established as an ionic radius (Pauling or Shannon-Prewitt) because it is an emergent result of microscopic processes, namely, to what degree water molecules can be wedged in between two ions on average.

3.5. To fit or not to fit?

Simplified models usually contain various parameters that are either accessible from fitting results to experiments, or they are obtained from experiments directly. In the calculation of thermodynamic data, basically, there are two routes. (1) One is to use adjustable parameters to reproduce experimental data. (2) The other is to minimize the number of adjustable parameters and to give up quantitative agreement with experiments. In this case, understanding physical mechanisms is in the focus and only qualitative agreement with experimental data is aimed for.

In our papers, we followed the second route; we did not use a single adjustable parameter in

our calculations. We used experimental or experimentally motivated (e.g., obtained from separate modeling procedures) parameters such as the solvation free energy, ΔG_i^s , the dielectric constant, $\epsilon(c)$, and the Pauling radii, R_i .

The agreement with experiments is qualitative (Fig. 2A), but the fact the sum of the large negative II term and the large positive IW term produces the right trend (Figs. 2B-D) justifies the basic idea of Hückel [9]. In the case of LaCl_3 the II and IW terms can be as large as $\pm 8kT$ which is a large value for two competing terms whose sum is supposed to reproduce a behavior in the $1kT$ regime. This is especially rewarding if we consider the fact that the II and IW terms are computed independently on the basis of very approximate models linked only through the $\epsilon(c)$ function. All these findings imply that the model contains the appropriate physics (at least to first order) of the complex behavior emerging from the interactions of ions and water molecules.

If we want quantitative agreement with experiments, we need to refine the model and to use adjustable parameters. If we have enough adjustable parameters, anything can be reproduced [145], so if want to preserve the explanatory power of the model, we need to keep the number of adjustable parameters to a minimum. This can be regarded as an application of Occam’s razor to this situation (“pluralitas non est ponenda sine necessitate” meaning that “plurality should not be posited without necessity.”).

3.6. Computation of the II term

The advantage of the decoupling of the II and IW terms is that we have some freedom to choose the computational method to estimate the II term. The only restriction is that the method must work on the basis of a model on the McMillan-Mayer level [146] using implicit solvent.

Here, we restrict ourselves to listing the various methods; for details the readers are directed to the original papers.

Debye-Hückel theory The first theory for the activity coefficient was developed by Debye and Hückel [7] whose extension to the case of a concentration dependent dielectric constant was first proposed by Hückel [9] in 1925 and later by Teitler and Ginsburg [10] in 1956 both assuming linear concentration-dependence of $\epsilon(c)$. The Modified PB theory of Outhwaite and Bhuiyan [147, 148] takes both volume exclusion and electrostatic correlations into account. A Corrected DH theory was proposed by Abbas et al. [17, 149–151], while the Extended DH theory was pro-

posed by Shilov and Lyashchenko [22–31]. Lately, a number of papers have been published by Kontogeorgis and several coworkers [32–41] using various versions of the DH theory and other methods.

Pitzer’s approach Pitzer’s approach [152–154] is based on the derivation of the osmotic coefficient from the virial relation using the DH pair distribution function. It is an extension of the DH theory and despite its simplicity it gives results in reasonable agreement with MC data. [155] This approach was used in various equations of state (EoS) as reviewed by Kontogeorgis et al. [89].

Mean Spherical Approximation This is one of the most extensively used theories beyond the DH theory. [156, 157] It’s conceptual elegance and structural simplicity made it a core component of DFTs and EoS’s. [34, 39, 59, 158] Gillespie et al. introduced the Mean Countershell Approximation (MCSA) by including the interactions between the ions and their screening clouds. [159] Høye and Gillespie proposed the Extended Mean Spherical Approximation (MSAX) [160] which is the original MSA supplemented with a previously ignored term for the excess chemical potential. The reasons why both theories are very accurate compared to MC simulations and physical interpretations of their terms have been analyzed by Gillespie [161] A recent analysis in comparison with Pitzer’s approach and MC has been published by Simonin and Bernard. [155]

Poisson-Fermi theory In an interesting theory of Liu and Eisenberg [19–21, 47], the concentration functions are bounded above thus attempting to take steric effects into account. They use a Fermi-like distribution to describe probability densities of water molecules in the hydration shell and outside of it. A spatial variation of the dielectric constant is also accounted for.

Monte Carlo simulations Computer simulations provide exact results for a given model apart from system size dependence and statistical uncertainty. [162–164] The two main classes are MC and MD simulations. MC simulations sample the configurational space stochastically [165] in equilibrium and provide ensemble averages for macroscopic thermodynamic quantities. MD simulations sample the phase space deterministically [166] and provide time averages. In equilibrium,

they give the same results for ergodic systems. MD simulations can also be used for non-equilibrium systems. While MC simulations are generally used for implicit-solvent models in equilibrium (out of equilibrium, the Brownian Dynamics method is the comparable tool), MD simulations are needed to simulate electrolytes in an all-atom explicit solvent framework.

MC simulations provide entropic quantities (chemical potential, free energies), if fluctuations in the number of particles are sampled in the simulation in some way. In the canonical ensemble (constant N , V , and T), MC simulations provide the chemical potential [17, 113, 150, 167] by applying Widom’s test particle method [79] by sampling the energetic consequences of inserting “ghost” particles in the simulation cell (Eq. 15).

A more appropriate ensemble is the grand canonical ensemble (constant μ_i , V , and T), because it allows the simulation of low concentrations. In this GCMC simulation, the chemical potentials are the independent variables, while concentrations of the various species are obtained as a result. [46, 168] In both ensembles, the simulation of individual activity coefficients imposed a challenge, see section 3.7 for more details.

MD simulations of explicit-water models are discussed in section 3.10.

Equations of State EoS’s contain various terms describing interactions of different types in the electrolyte. [18, 39, 40, 54, 59, 84–90] These interactions include those of the screened II interactions (treated by a theory or simulation discussed above), solvation (treated typically by the Born-theory [8, 36, 41, 48, 54, 169]), and ionic association [34, 85, 89, 90, 109, 110, 170, 171]. EoS’s have many adjustable parameters, but they are developed with the ambition of covering the entire thermodynamics of electrolyte systems, not only activity coefficients. The non-monotonic behavior of the activity coefficient, however, is such a characteristic property involving competition of terms of different signs that it is a natural expectation from EoS’s that they should be able to reproduce this behavior.

In general, molecular simulations (MC and MD) have the advantage of producing accurate results for a given molecular model. Their disadvantage is that they are lengthy and relatively difficult

to implement, although with the development of computers and user-friendly simulation packages this has been becoming less of a problem. Theories always contain approximations in solving the statistical mechanical problem for a model. In the case of a theory, therefore, two kinds of errors are present: error in the model and error in the method. In simulations, the second kind of error is absent.

When we apply an admittedly oversimplified model such as the electrolyte models on the McMiller-Mayer level, errors in the model are necessarily present. Such coarse-grained simple models usually contain adjustable model parameters and macroscopic quantities used at the nanoscale (e.g., dielectric constant). If we need to fit parameters anyway, using easy-to-use theories might be worthwhile as soon as they contain all the relevant physics to interpret the problem qualitatively despite being quantitatively inaccurate. If important degrees of freedom are missing in the theory, the application of computer simulations or better theories is needed. Typical examples are ionic correlations in multivalent electrolytes at high concentrations, where charge inversion and other interesting phenomena are missed by mean-field theories (see more about this in section 3.8).

3.7. Individual activity coefficient

Even recently there has been a heated debate in the literature not only about the measurability of individual activities, but also about the mere existence of these quantities. This debate goes back to the old days with Guggenheim [172–174] and Taylor [175] stating that activity has “no physical significance for a single ion species”, while Lewis [60], Harned [176], and Brønsted [177, 178] accepting that the individual activity is a thermodynamically well-defined quantity for charged species.

From the point of view of an experiment in which the chemical potential is determined from the free energy change upon adding a mole ions of a given species to a solution, the individual excess chemical potential is not possible. If one also adds the appropriate amount of counterions, the mean activity is the result.

The chemical potential of a charged species, however, can unambiguously be defined as a partial molar quantity in the thermodynamic limit, where charge imbalance vanishes:

$$\mu_i = \lim_{V \rightarrow \infty} \left(\frac{\partial F}{\partial n_i} \right)_{T, V, n_j \neq n_i} . \quad (18)$$

Since this is possible to approximate in computations, the individual chemical potentials were cal-

culated in many works with comparison to MC results. [148, 179–192]

Comparison with experimental data, however, requires measurements of the individual activity coefficients. While early papers were published on this matter [193–196], a revival of these measurements started with the work of the group of Vera and Wilczek-Vera (VWV) [73, 197–216] followed by other authors [217–221]. These experiments generally deduce the activity coefficient from measurements for an electrochemical cell containing ion selective membrane electrodes [73, 197–215, 217–221], ion selective glass electrodes [193, 220], or electrodes of the second type [193–196]. A problematic part of these measurements is the appearance of a junction potential whose estimation requires some theoretical consideration such as Henderson’s equation [222, 223] or any of its modifications [73, 176, 224, 225].

The works of VWV generated a heated debate in the literature [207, 208, 212–216, 226–235] Malatesta [226–229] and Zarubin [231–233] being the main opponents.

From our part, we not only believe that individual activities are valid thermodynamic quantities whose measurements would deserve more effort, but we believe that they are extremely important. We mention just two examples to support our statement.

(1) If a single ionic species establishes chemical equilibrium between two phases, the individual activities cannot be avoided. In the case of the Donnan membrane equilibrium, a semipermeable membrane separates two baths of different compositions for which the cell membrane is the typical example where K^+ -selective ion channels make the membrane permeable for K^+ ions in its resting state. At an electrode-electrolyte interface the dynamical equilibrium of oxidation and reduction processes establishes the resting state. The equilibrium electrode potential often depends on the activity of just one ionic species.

If a charged object (surfaces, macromolecules, chemical groups) is present in adjacent with the electrolyte, cations and anions are separated and distinguished, so the mean activity cannot be used if we want to describe the equilibrium of this interfacial region with the bulk. In fact, the recent MCSA and MSAX theories [159, 160] show that the individual cation and anion activity coefficients needed to describe this system have large contributions that cancel in the mean activity coefficient.

(2) If the system is out of equilibrium, transport processes occur spontaneously, where the drift-diffusion of a single ionic species is driven by the gradient of its individual chemical potential, see

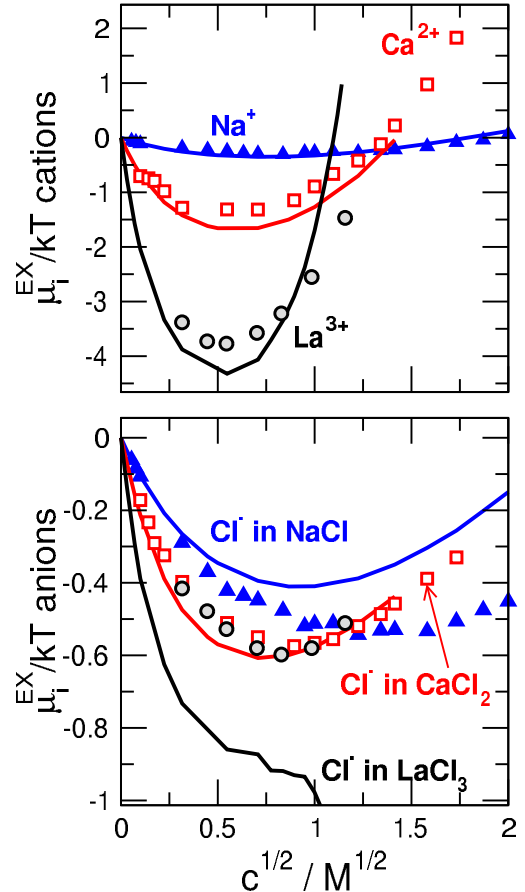


Figure 3: The individual excess chemical potentials ($\mu_i^{\text{EX}}/kT = \ln \gamma_i$) as functions of concentration for NaCl, CaCl_2 , and LaCl_3 (blue, red, and black colors) as obtained from experiments (symbols) [73, 77] and the II+IW theory (lines). The top and bottom panels show the cation and anion activity coefficients, respectively. For more details see the caption of Fig. 2. The results are from Refs. [5, 6]

the Nernst-Planck (NP) equation:

$$\mathbf{j}_i(\mathbf{r}) = -\frac{1}{kT} D_i(\mathbf{r}) c_i(\mathbf{r}) \nabla \mu_i(\mathbf{r}), \quad (19)$$

where $\mathbf{j}_i(\mathbf{r})$ is the flux density profile, $D_i(\mathbf{r})$ is the diffusion coefficient profile, $c_i(\mathbf{r})$ is the concentration profile, and $\mu_i(\mathbf{r})$ is the chemical potential profile. In neither of these cases can the individual activities be replaced by the mean activities.

Even if we accept the replacement of individual activities with mean activities as a good idea, this is an acceptable approximation only for 1:1 electrolytes, as shown in Fig. 3 where both Na^+ and Cl^- have individual excess chemical potentials in the same ballpark ($\approx -0.5kT$). For multivalent electrolytes, this replacement is far from being applicable. The top and bottom panels of Fig. 3 show the cation and anion activity coefficients, respectively, for NaCl, CaCl_2 , and LaCl_3 as obtained from the II+IW theory (curves) in

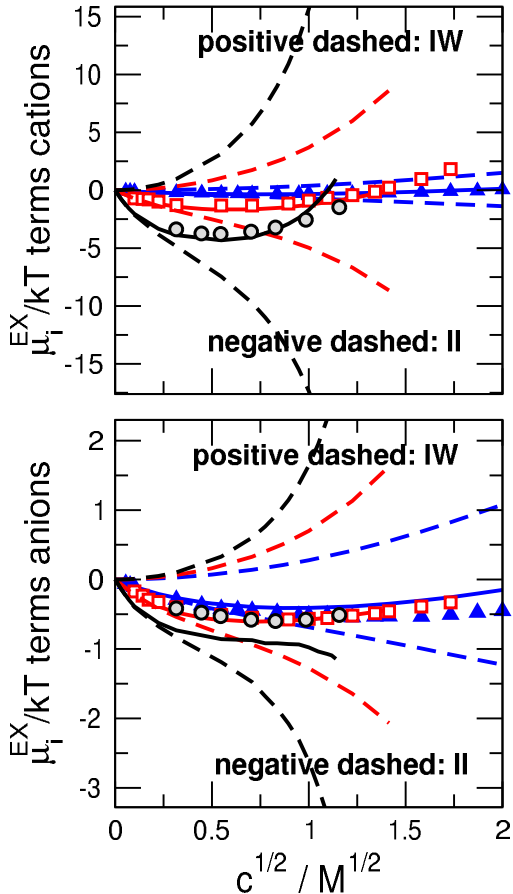


Figure 4: The individual excess chemical potentials and the II and IW components ($\mu_i^{\text{EX}} = \mu_i^{\text{II}} + \mu_i^{\text{IW}}$) as functions of concentration for NaCl, CaCl₂, and LaCl₃ (blue, red, and black colors) as obtained from experiments (symbols) and the II+IW theory (lines). The top and bottom panels show results for the cation and anion, respectively. The solid lines show the total excess term (these are the same as in Fig. 3), while the dashed lines show the IW and II terms. Dashed lines above the solid lines (positive) refer to the IW term, while dashed lines below the solid lines (negative) refer to the II term. For more details see the caption of Fig. 2. The results are from Ref. [5, 6]

comparison with experimental data (symbols).

The II and IW terms are shown in Fig. 4. The same conclusions can be drawn as for the mean values (Figs. 2B-D): the balance of a large negative II term with a large positive IW term produces the non-monotonic behavior of the EX term in qualitative agreement with experiment. The case of La³⁺ is especially impressive: in the $c=0$ to 1 M concentration range the IW and II terms vary in the range $\approx \pm 15kT$ producing the variation of the EX terms in the 0 to $\approx -4kT$ range.

Note that handling multivalent electrolytes with theories becomes difficult at large concentrations due to strong electrostatic correlations (see section 3.8). In these cases, the application of MC simulations is advantageous. We used

GCMC simulations, in which the chemical potential is the independent variable, while the concentrations are the output results. Traditionally, GCMC simulations of electrolytes were performed preserving charge neutrality since Valleau and Cohen [168]. This means that neutral groups of cations and anions (ν_+ cations and μ_- anions) were inserted to and deleted from the simulation cell; the salt concentration was the output of the simulations.

It was also around 2010 [236] that we gave up instantaneous charge neutrality in the simulation cell and allowed charge fluctuation by inserting/deleting individual ions. While charge neutrality is a requirement at the macroscopic scale, the fluctuation of charge on the microscopic level not only allowed but realistic. In that paper [236] we also suggested an iterative method (Adaptive GCMC, A-GCMC) to determine chemical potentials corresponding to prescribed ionic concentrations. We used this method to obtain the results shown in this paper.

We get the the individual excess chemical potential of an ionic species with a systematic error using the Widom test particle method (Eq. 15) due the violated charge neutrality in a finite system when inserting individual ions. Sloth and Sørensen developed a correction formula on the basis of a neutralizing background [186]. They assumed that the missing charge, Q , is smeared over the cubic simulation cell ($V=L^3$) as a constant volume charge of magnitude Q/V . The interaction of an inserted ion, q , with this neutralizing background can be integrated as

$$\mu_Q^{\text{corr}} = -\frac{qQ}{32\pi\epsilon_0\epsilon L}K, \quad (20)$$

where K is a constant. When we insert a single ion in a charge neutral solution, $Q=-q$. The correction term scales with L^{-1} , so it goes to zero as the size of the system approaches infinity. Note that this correction term is used in our A-GCMC method. [236] Svensson and Woodward [237] proposed a different correction method.

The idea of giving up instantaneous and local charge neutrality led us to thinking locally. While MC simulations were designed and used for global equilibrium (via the ergodic hypothesis), we decided to give up global equilibrium too and to assume local equilibrium only. So we developed the Local Equilibrium Monte Carlo (LEMC) method [134, 135, 238] that can also be used out of equilibrium (but in steady state) by coupling it to the NP equation (Eq. 19).

In this hybrid method (NP+LEMC), we divide the simulation cell into small volume elements

where we assume local thermodynamic equilibrium by setting the local chemical potential, e.g., the chemical potential profile, $\mu_i(\mathbf{r})$. GCMC insertion/deletions are performed by using the local chemical potential. The result of the simulation is the concentration of each ionic species in each volume element, e.g., the concentration profile, $c_i(\mathbf{r})$. Thus, we establish a relationship between $\mu_i(\mathbf{r})$ and $c_i(\mathbf{r})$. The NP+LEMC method produces a self consistent system, where the profiles satisfy the NP equation and the continuum equation. It is evident that such a method could not be developed without working with individual ions and their chemical potentials.

3.8. Multivalent electrolytes

Multivalent ions ($|z_i| > 1$) impose a special challenge for electrolyte theories partly because the interactions between ions are stronger, partly because the asymmetry in ionic charges (2:1, 3:1 systems) introduces ionic correlations that are not present in symmetric systems. Charge inversion and overcharging are associated phenomena that are at the core of many experimental observations and modeling efforts. [126, 135, 239–262]

The basis of the phenomenon is that multivalent ions attract so strongly to charged objects that they overcharge them, namely, more counterions are attracted to these charged objects than the amount needed to neutralize them. This changes the apparent charge of the object resulting in interesting phenomena such as the appearance of a layer of excess coion and change in the sign of the potential (charge inversion). The charged object can be many things, from metal electrodes to insulating materials with surfaces containing charged chemical groups (macromolecules, membranes, basic materials of nanofluidic devices).

Because the most interesting applications occur in inhomogeneous systems in biological, electrochemical, and nanotechnological devices, the correct modeling of multivalent ions in such systems is essential if we want to understand the mechanisms underlying the functioning of these devices. Because electrolyte baths are always present in these systems, the correct modeling of bulk electrolytes is the starting point. This means that mean-field theories should be used with caution in such cases.

3.9. Temperature dependence

While most of the activity measurements were performed for room temperature (298.15 K), we found experimental data for $\epsilon(c, T)$ [69–71, 91–93] and $\gamma_{\pm}(c, T)$ [61] of NaCl (the temperature dependence of ΔG_i^s is small and ignored [263, 264]).

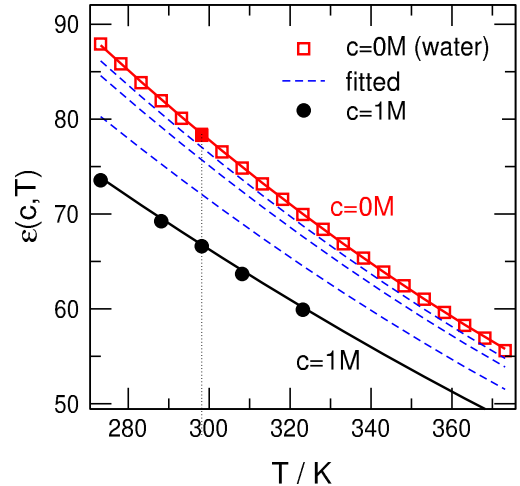


Figure 5: Temperature dependence of the dielectric constant of NaCl solutions. Symbols denote experimental points, while curves denote interpolations/extrapolations obtained from Eq. 21. Squares denote experimental data for water [61]. For $c=1$ M, the data of Pottel *et al.* [92, 93] (filled circles) are shown. They are in good agreement with the data Buchner *et al.* [69] for $c=1$ M and $T=298.15$ K. The blue dashed lines are fits for $c=0.1, 0.2,$ and 0.5 M (from top to bottom) as described in the text. The results are from Ref. [3].

In a detailed study of NaCl, we proposed the following fit for the dielectric constant on the basis of experimental data for $c \rightarrow 0$ [69] and $c=1$ M [92, 93]:

$$\epsilon(c, T) = \epsilon(c, T_0) + \alpha(c)(T - T_0) + \beta(c)(T - T_0)^2, \quad (21)$$

where $T_0 = 298.15$ K, $\epsilon(c, T_0)$ is given in the caption of Fig. 1, and the coefficients $\alpha(0) = -0.35596 T^{-1}$, $\alpha(1) = -0.27359 T^{-1}$, $\beta(0) = 0.00071466 T^{-2}$, and $\beta(1) = 0.00037564 T^{-2}$. We obtained the $\alpha(c)$ and $\beta(c)$ values between 0 and 1 M with a linear fit. Our fitted functions are plotted for $c=0.1, 0.2,$ and 0.5 M as dashed blue lines in Fig. 5.

Figure 6 shows the mean excess chemical potential of NaCl for $c=0.2$ M. The results are obtained in three different ways.

- The value of the dielectric constant is fixed at $\epsilon_w = 78.45$ (the value for water at room temperature; filled red square in Fig. 5). The IW term is zero in this case. The II term depends on temperature through the acceptance probabilities of the MC moves.
- The dielectric constant is T -dependent, but not concentration-dependent, namely we use the dielectric constant of water, $\epsilon_w(T)$. The IW term is zero in this case too. The II term depends on T not only through the acceptance probabilities of the MC moves, but also

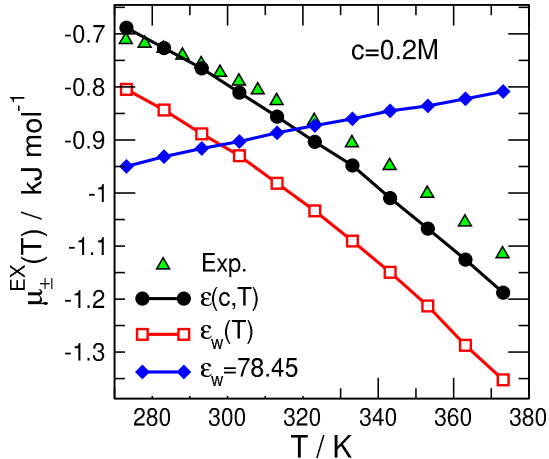


Figure 6: Temperature dependence of the mean excess chemical potential $\mu_{\pm}^{\text{EX}} = RT \ln \gamma_{\pm}$ of NaCl for $c=0.2$ M compared to experimental data [61]. Different curves are obtained from different calculations by assuming different concentration and/or temperature dependence for the dielectric constant (for details, see the text). The results are from Ref. [3]

by the changing $\epsilon_w(T)$ in the denominator of Eq. 7.

- Both the c - and T -dependence of the dielectric constant is taken into account, $\epsilon(c, T)$, through Eq. 21. For details, see Ref. [3].

The main conclusion of the result is that the dependence of the dielectric constant on both state variables (c and T) should be taken into account. For a constant value, $\epsilon_w=78.45$, even the trend of the T -dependence is wrong. Using the water dielectric constant, $\epsilon_w(T)$, gives the correct trend but the curve is shifted compared to the experimental curve. This shift is corrected by using the full $\epsilon(c, T)$ function.

3.10. Explicit-water molecular dynamics simulations

Although the focus of this work is primarily on implicit-solvent models, MD simulations of all-atom models using explicit water are vital. In these models, ions are usually Lennard-Jones particles with point charges in their centers, while a wide variety of water models is available whose discussion is well beyond the scope of this paper. Here, we just mention the papers of a couple of research groups who produced chemical potential calculations in their MD simulations.

Chemical potential and free energy calculations are problematic in high-density electrolytes. This has been solved by developing special techniques such as thermodynamic integration and osmotic ensemble. Chemical potential has been computed

for a while in solubility studies [141, 265–269, 269–273] because explicit-water MD is easier to perform at large ionic concentrations. Mean activity coefficients have been reported by Joung et al. [144, 274], Benavides et al. [275, 276], Mester and Panagiotopoulos [277, 278], and Young and Panagiotopoulos [279, 280]. We are aware of only one work on individual activity coefficients by Saravi and Panagiotopoulos. [281]

All these studies, however, are not more accurate than their implicit-water counterparts when comparing to experimental data. This is probably the consequence of force fields for ions and water that are mainly rigid ignoring polarization. The advantage of these studies is that we gain insight into molecular mechanisms that are coarse-grained in the implicit-water models.

4. Summary

In this work, we summarized our II+IW theory by discussing several issues associated with it. Our purpose with the discussion was to put the main elements of the theory on the table, clarify their relationships with each other, present difficulties, and emphasize strengths.

4.1. Limitations of the theory

We consider the II+IW theory both powerful and insightful, but it does have limitations: in its present form it is designed for estimating the activity coefficients of the ions. There is more to electrolytes beyond ions, however, and more to thermodynamics than activities.

Water is just a background in our approach. Although its activity coefficient can be deduced via the Gibbs-Duhem equation [22], water has a decisive contribution to pressure whose calculation is beyond implicit-water models. A full thermodynamic picture, therefore is not provided by the theory.

Although we considered it an advantage to decouple the II and IW terms so far it is no doubt a simplification. Simplifications are useful when trying to keep the computational complexity to a minimum by reducing the number of explicit degrees of freedom, but they become an obstacle to accuracy and deeper understanding at a given point. In this case, that point is the implicit solvent model itself whose mere purpose is to “get rid” of water in some sense.

4.2. Merits of the theory

The theory is, however, successful in its limited scope despite its lack of corpuscular solvent: it qualitatively reproduces the individual activity

coefficients of cations and anions even in multivalent electrolytes where the difference between these activity coefficients can be very large. The temperature dependence of the activity coefficient is also well reproduced. All these are done without a single adjustable parameter. Instead, we have substituted both hard experimental data and a hypothesis of how the hydration contribution to the activities changes with ion concentration and temperature (Eq. 12). The theory can be straightforwardly generalized to electrolyte mixtures, as well as solvent mixtures, as soon as measurements or predictions for the composition dependence of the dielectric constant are available.

Conceptual simplicity and the resulting physical insights are merits of the theory from a practical point of view. Electrolytes are useful when they are at work in biological and technological devices, namely, in inhomogeneous and non-equilibrium systems. Such systems are much harder to treat with explicit-water MD, so if we have a good functional model for a bulk electrolyte, we are making a major step towards modeling such devices.

The applicability of such models is limited, however. In these devices, the ions travel between bulk phases via pores or they are adsorbed into materials from the bulk phases. The dielectric constant may be quite different in the respective subsystems (pore, membrane, electrode, bulk, etc.). In such cases, ions may cross dielectric boundaries which poses many computational problems. [83, 282] All-atom MD simulations are indispensable in such cases.

4.3. Take home message

The theory has a well-defined core idea, the concentration dependent dielectric constant, that goes beyond computing activities like we go here. It can be used in approaches that are more complete than the II+IW theory like equations of state.

Fundamentally, we use an additional experimentally attainable parameter and propose to take solvation into account with Eq. 12 (and how it defines temperature and concentration dependence) rather than with an increased ionic radius at a fixed dielectric constant. These are two competing concepts that work at practically the same level of resolution (MacMillan-Mayer). In our view, two very strong pieces of evidence support the II+IW idea:

1. It is an experimental fact that the dielectric constant changes with concentration.
2. The artificially increased size of ions excludes configurations from the sample that are of

extreme importance near saturation, namely those when ions come into contact and associate.

These same arguments are also fundamental to the development of equations of state. This aspect of electrolytes is then at a crossroads, and serious consideration is required about which path to choose.

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