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Insight into the ionic atmosphere effect: Comparison of theories for electrolytes at the primitive level

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Abstract

In their seminal paper of 1923, Debye and Hückel provided the first appropriate description of the effect of ionic strength on the thermodynamic properties of dilute electrolyte solutions. This landmark work paved the way for what was later called the primitive model of electrolytes. At this level, an ionic solution is modeled as a collection of charged hard spheres in a dielectric continuum that manifests itself only through its dielectric constant. Numerical simulations have been reported in the literature for salts in a continuous solvent. In the present work, results obtained using various analytical theories are compared with Monte-Carlo (MC) simulation data (expected to be ‘exact’) taken from the literature, in the case of binary electrolytes in a continuous solvent mimicking water. The theories include the Debye-Hückel theory, the mean-spherical approximation (MSA), and the Pitzer approach. The MC data are about mean salt activity and osmotic coefficients, and also individual ion activity coefficients. Moreover, some remarks are made about the assumptions underlying the Debye-Hückel framework, and new formulas are derived for individual ion activity coefficients by following the method of Pitzer.

Keywords: Electrolytes, Debye-Hückel, Mean Spherical Approximation (MSA), Thermodynamics.

1. Introduction

This paper was written for the 100th anniversary of the publication of the landmark work by Debye and Hückel in 1923 [1], for which two English translations are available [2, 3].

During the past century, the theory of electrolyte solutions has experienced an impressive development, with the advent of analytical models, numerical solutions to integral equations, and numerical simulations [4, 5]. The work by Debye and Hückel (DH) provided the cornerstone for the blooming of this research, aimed at a description of the structural and thermodynamic properties of ionic solutions. A renewed interest in this theory has been observed in the past decade, per se [6–9] and in applications in the field of chemical engineering [10, 11].

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A number of works has been published [6, 9] praising comparable merits for the DH theory and the MSA, and with the purpose of rehabilitating the DH work in the field of electrolyte thermodynamics. One has to admit, though, that the DH theory is now generally regarded as an outdated tool for the modeling of deviations from ideality. Shortly after the DH publication of 1923, it appeared necessary to complement the DH thermodynamic equations for electrolyte solutions, by adding a corrective term proportional to the salt concentration [12–16]. Later on, as in Pitzer’s work [17, 18], a polynomial in powers of concentrations was added in order to better describe the deviations from ideality.

Clearly, real electrolytes are not made up of charged hard spheres in a continuum. Besides charge and short-range repulsion, many other specific interactions characterize ions in solution [19–21]. The corrective terms added to the original DH expressions allowed one to represent the influence of these effects, and also to compensate for shortcomings in DH expressions. This kind of correction cannot be easily related to individual ion physical properties. The added parameters were adjusted on experimental data for the various quantities studied. The description of mixtures requires additional parameters. On the other hand, in more recent molecular thermodynamic models and in simulations, solutions are described by considering explicitly the effect of solvent molecules. Electrostatic contributions are no longer simply introduced using adjustable parameters but it is attempted to relate them more closely to the interactions between the species.

Another analytical theory that has been popular in the chemical engineering community is the mean-spherical approximation (MSA). It was proposed initially by Percus and Yevick in 1964 [22] and Lebowitz and Percus in 1966 [23]. It was subsequently first solved by Waisman and Lebowitz in 1972 [24, 25], and developed mainly by Blum [26]. It shares with the DH approximation the property of being a linearized theory, and of giving analytical expressions for the deviations from ideality in electrolyte solutions. These expressions are similar in form to the DH ones. However, as will be seen below, the MSA was introduced as a refinement over the DH theory by accounting in a better way for the effect of the excluded volume of the ions on the correlation functions. At low concentration, it yields numerical results that are very close to those obtained from DH. At high concentration, the steric repulsion between the ions is expected to modify their distribution and the screening length. Furthermore, as required by some general rules [27–29], the distribution functions should no longer have a simple monotonic decreasing variation with distance but they should exhibit oscillations. This phenomenon is not described by DH theory, but it is observed within the MSA [26], which is a satisfactory outcome.

The above models have been extensively used for accurate representations of deviations from ideality for electrolytes in water and organic solvents at various temperatures (and sometimes pressures) as, e.g., in Refs. 30–32 for the DH theory, in Refs. 17, 18, 33 for the Pitzer approach (generally up to 6 mol kg^{-1}), and in Refs. 34–39 for the MSA.

Other available methods deserve being mentioned in this background, namely the hypernetted-chain (HNC) approximation [40] (which involves a numerical resolution) and Pitzer’s approach [17, 41].

Pitzer’s approach has the advantage of being developed directly from the DH pair distribution functions $h_{ij}(r)$. It differs from that of DH by the way in which the thermodynamic quantities are obtained. It is therefore a direct extension of DH theory. However, a drawback is that, in the latter, the screening length $1/\kappa$ in particular does not depend on the shape and size of the ions present in the ionic atmosphere around a given ion.

The DH theory and its improvements deserved a renewed consideration of their capabilities. This is one of the purposes of this special issue.

Moreover, Monte-Carlo (MC) numerical simulations have been carried out since 1970 [42–48]. In Ref. 47, ion sizes were determined to reasonably reproduce experimental mean activity and osmotic data, and individual ionic activity coefficient values computed using these sizes were reported. The MC method is expected to provide ‘exact’ results for the activity and osmotic coefficients computed at the primitive level. The comparison with the osmotic or activity coefficients resulting from simulations with continuous solvent allows one to evaluate the limits of application of various analytical theories.

We note that, in these simulations, the permittivity of the solution is considered not to vary with concentration. Of course, this is not the case in real electrolytes. The relative permittivity of ionic solutions, ε_{sol} , is experimentally known to vary (generally decrease) with salt concentration [49]. However, ε_{sol} contains dynamic contributions that are difficult to estimate [50, 51]. Therefrom, uncertainties remain about the value of the ‘static’ permittivity of real electrolytes, that is needed in models for electrolytes.

The variation of solution permittivity with solute concentration has been taken into account in models for a long time. The influence of this variation on the activity coefficient of ions was already recognized in 1925 in a work by Hückel [12] within DH theory. In the latter framework, the inclusion of this effect has experienced a renewed interest in the recent literature [7, 52]. Within the MSA, it started being taken into account in a paper by Triolo et al. in 1977 [53]. Then, it has been used extensively in subsequent studies using the MSA [37, 54–57]. In Refs. 37, 54, 55, experimental data for ε_{sol} were not taken because of the above-mentioned uncertainty on the magnitude of the static permittivity, and also because ε_{sol} is a *macroscopic* quantity. Thus, it cannot be employed to describe interactions at short interionic distances [37], where these interactions are besides strongest.

In this study, the solution permittivity is taken constant, equal to that of water, as in the MC simulations.

The main purpose of the present work is to examine more carefully the accuracy of the above mentioned theories for the description of deviations from ideality at the primitive level of ionic solutions. This is achieved by comparing the values of mean salt activity and osmotic coefficients, as well as individual ion activity

coefficients, obtained from these theories with MC results in the case of monovalent, as well as multivalent, electrolytes of one single salt [47, 48]. This systematic comparison gives an idea of the impressive span of the various methods that have been developed since the publication of the seminal work by Debye and Hückel. It also provides a clarification of the respective capabilities of the available theories for the description of deviations from ideality in ionic solutions. Let us underline that this comparison is done without introducing any adjustable parameter in the theories. The present analysis is carried out at the primitive level at which the ions are characterized by their individual size and charge, and the solvent by its dielectric constant. At this level, in order to compare the results from various theories with those from MC simulation, it is necessary to add a contribution from excluded volume to the electrostatic part of the deviations from ideality. This is done by using the Mansoori-Carnahan-Starling-Leland formulas [58], which are known to be very accurate for the volume fractions studied here in the simulations.

The structure of this article is as follows. In the next section, the various theories considered in this work are presented, together with a short preliminary presentation of the context in which these primitive level models may be used. New results are obtained within Pitzer’s framework in the case of ions of different sizes. Then, the results obtained from the models are presented and compared with MC data. Finally, some remarks and prospects are presented in the conclusion.

2. Theories for electrolytes at the primitive level

This section is devoted to a brief summary of the theories considered in this work. Their main features are expounded and the main equations used hereafter are given.

The models presented in this section are built at the primitive level, in which an ionic solution is modeled as a collection of ions, regarded as charged hard spheres, embedded in a continuum dielectric representing the solvent (water in this work). The latter is assumed to manifest itself only through its dielectric constant. The ions are assumed to be free (strong electrolyte).

The diameter of an ion will be σ_i and the minimum distance of approach of two ions i and j will be

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (1)$$

Since the ions are modeled as hard spheres, the thermodynamic quantities split up into two contributions, for the HS and electrostatic parts. So one has for the Helmholtz energy,

$$A = A^{HS} + A^{el} \quad (2)$$

where the superscripts ‘HS’ and ‘el’ indicate hard sphere and electrostatic contributions, respectively. Hereafter, the electrostatic contribution will be described using three different theories, namely Debye-Hückel, Pitzer, and MSA.

In the same way, the activity and osmotic coefficients can be broken down as,

$$\ln \gamma_i = \ln \gamma_i^{HS} + \ln \gamma_i^{el}, \quad \Phi = \Phi^{HS} + \Phi^{el} \quad (3)$$

The same HS contribution was added to the three electrostatic ones for a comparison with MC data. The expressions used for the HS contributions are given in Appendix A.

The mean activity coefficient of a salt S in a binary solution is given by,

$$\ln \gamma_S = \frac{1}{\rho_t} \sum_k \rho_k \ln \gamma_k \quad (4)$$

$$= \frac{1}{\nu_+ + \nu_-} (\nu_+ \ln \gamma_+ + \nu_- \ln \gamma_-) \quad (5)$$

where ρ_i is the number density of ion of type i (number of ions per cubic meter), $\rho_t = \sum_i \rho_i$, and ν_+ and ν_- are the stoichiometric numbers of cation (+) and anion (-) of salt S, respectively.

In addition, the contribution from electrostatic interactions to the osmotic coefficient Φ^{el} is given by the relation [54],

$$\Phi^{el} = \ln \gamma_S^{el} - \frac{\beta A^{el}/V}{\rho_t} \quad (6)$$

2.1. The McMillan-Mayer level

It may be useful to give some precisions about the level of description of the models considered here.

All models in which the solvent is taken as a continuum are in fact developed at the McMillan-Mayer (MM) level [59]. These authors extended the brilliant analogy first highlighted by van't Hoff [60], between a dilute solution and a gas of solute, to the case of concentrated solutions viewed as an imperfect gas. In this framework, the chemical potential of the solvent is maintained constant by applying on the solution an additional pressure which is equal in magnitude to the osmotic pressure of solution. The ions interact through *effective* forces that are averaged over the states of the solvent. The corresponding interaction potentials are the potentials of mean force between the ions at infinite dilution in the solution [59, 61]. Hence, assuming that these potentials are those for hard cores, as is done at the primitive level, is clearly a great simplification. Nevertheless, the effect of hydration shells can be translated into ion sizes being larger than their crystallographic diameters. On this basis, it is hoped that this type of model at MM level can be able to capture the main features of an ionic solution.

The thermodynamic properties of an ionic solution at MM level have to be converted to the experimental level (constant pressure), also called Lewis-Randall (LR) level [4, 62, 63]. We now take the opportunity of this work to touch briefly upon the question of this MM-to-LR conversion.

The necessity of applying the conversion to the activity and osmotic coefficients obtained at MM level for comparison with experimental data may be seen from the simple following remark. Let us denote by γ_S^{MM}

the MM activity coefficient of salt S . It is defined on a molarity basis: $\gamma_S^{MM}(C_S)$, where C_S is the molar concentration of S . For comparison with experimental data, γ_S^{MM} first needs to be converted to a *molality* basis by using the classical formula,

$$g_S^{MM} = \gamma_S^{MM} \frac{V_W}{V_S} \quad (7)$$

where g_S^{MM} is the mean salt MM activity coefficient on molality scale, V_S is the specific volume of solution (volume of solution per kg of solvent), and V_W that of pure solvent ($V_W = 1/d_W$ with d_W the density of pure solvent).

The activity and osmotic coefficients at MM level, γ_S^{MM} and Φ^{MM} fulfill the Gibbs-Duhem relation. Clearly, this is not so for g_S^{MM} and Φ^{MM} because g_S^{MM} is not equal to γ_S^{MM} .

So, how can one have an osmotic coefficient that will be thermodynamically consistent with an activity coefficient on molality scale?

The answer to this question is that this is precisely the role of the MM-to-LR conversion. This conversion yields coefficients g_S^{LR} and Φ^{LR} that satisfy the Gibbs-Duhem relation [4, 62, 63].

So, the conversion is required when one wants to compare the results of theories constructed at MM level (that is theories in which the solvent is a continuum) with experimental data. The magnitude of the MM-to-LR conversion was studied for a number of salts of various stoichiometries [4, 63]. Explicit expressions, relating g_S^{LR} and Φ^{LR} to g_S^{MM} and Φ^{MM} , can be found in these latter references.

No conversion will be needed in this work because the MC data are obtained for primitive electrolytes at MM level.

2.2. The Debye-Hückel theory

The DH theory [1–3] is well known. Excellent accounts have been published in the literature [19, 64], that will not be repeated here. However, it may be useful to point out some important features of the theory.

A simple, yet fundamental, element of the theory is that it singles out a particular ion that is held fixed. The distribution of ions around this ‘central’ ion is determined by considering that these ions are placed in an electric field obeying Poisson’s equation of electrostatics. The local density of charge at some point in the ionic cloud is assumed to be governed by a Boltzmann distribution, which involves the electrostatic potential for this field. Therefore, this potential fulfills a self-consistent equation: the ions in the cloud are distributed according to an electrostatic potential created by the ions themselves. This method of resolution makes the DH approximation a *mean-field* theory. The first theory of this type was introduced by P. Weiss in 1907 for a description of ferromagnetism [65]. Another similar mean-field approach was used by Hartree in 1927 [66] when solving the problem of an assembly of electrons in quantum mechanics by using the Schrödinger equation.

In DH approximation (as well as in other primitive models), it was further assumed that the interior of the ions is made up of a medium of the same permittivity as the solvent [1–3], which avoids having to consider possible polarization effects at the ion surface. Moreover, every type of ion, when it is taken as central ion, is characterized by a minimum distance of approach for the surrounding ions. It was realized by Debye and Hückel that this distance includes a “firmly attached layer of water molecules”.

These comments show that the DH approximation involved in fact a rather elaborate treatment with various levels of approximations. This seminal paper led them to the result that deviations from ideality scale as $C_S^{1/2}$, not $C_S^{1/3}$ as previously proposed by Milner [67] and Gosh [68]. Overall, one is impressed by the elegance and relative simplicity of the demonstration expounded in DH paper, which arrived at this counterintuitive finding.

The DH treatment revealed the existence of a characteristic screening length for the potential around an ion, given by $1/\kappa$, where κ is the Debye screening parameter given by,

$$\kappa^2 = 4\pi \lambda \sum_i \rho_i z_i^2 \quad (8)$$

in which z_i is the valence of ion of type i , $\lambda = \beta e^2 / (4\pi \epsilon_0 \epsilon_W)$ is Bjerrum distance, $\beta = 1/k_B T$ (k_B being Boltzmann constant and T the temperature), e is elementary charge, ϵ_0 is the permittivity of a vacuum, and ϵ_W is the dielectric constant of water (=78.4 at 25°C).

The expression for the DH Helmholtz energy A^{DH} , and mean activity and osmotic coefficients are given in Appendix B.

It was stated in DH paper [1–3] that the minimum distance of approach to ion i , a_i , “constitutes the mean value for the distance to which the surrounding ions, positive as well as negative, can approach the singled-out ion”. A similar definition was given by Hückel later in 1925 [12]. In subsequent literature, a common value for a_i has often been taken (an adjustable mean distance of approach, or the average diameter of the ions [13]). Sometimes, the individual diameter σ_i has been used for a_i [69].

This distance is a key parameter in DH theory (and in this work), but its precise value is not easy to specify. In a dilute to moderately concentrated solution, a_i should rather be the mean approach distance of *unlike* ions to ion i because this ion interacts mostly with ions of opposite charge in such solutions. Ions of like charge are repelled by ion i , so it would make little sense to include them in the mean distance of approach. Thus, in a binary solution containing one salt made up of two ions, the distance of closest approach will be the same for the two ions.

In concentrated solutions, ions of like charge would get closer to ion i but using the DH theory for such solutions would become risky. We note that this question has been the subject of discussions in the case of salt mixtures [70–72].

When the salt concentration is increased in real solutions, the variation of the solution permittivity also plays a role as was recognized by Hückel [12]. This variation has an effect on the activity coefficient of ions in DH theory, that has been studied recently [7, 52].

2.3. Pitzer's approach

We now present the theory derived by Pitzer from the DH model. This theory differs from the latter only by the way in which the thermodynamic quantities are obtained. Instead of determining the electrostatic Helmholtz energy by thermodynamic integration of the electrostatic internal energy E^{el} , the osmotic coefficient is first found using the virial relation. Therefrom, the Helmholtz energy and the mean activity coefficient can be obtained. By using this route, statistical mechanics provide an alternative way for obtaining thermodynamic quantities for charged hard spheres [64]. One has,

$$\Phi_{virial}^{DH} = \frac{\beta E^{DH}/V}{3\rho_t} + \frac{2\pi}{3\rho_t} \sum_{i,j} \rho_i \rho_j \sigma_{ij}^3 h_{ij}(\sigma_{ij}) \quad (9)$$

where $\beta E^{DH}/V$ is the electrostatic internal energy obtained within the framework of the DH theory. It may be obtained as follows.

The general relation for the electrostatic internal energy E^{el} is,

$$\beta E^{el}/V = 2\pi\beta \sum_{i,j} \rho_i \rho_j \int_{\sigma}^{\infty} V_{ij}^{el}(r) h_{ij}(r) r^2 dr \quad (10)$$

where $V_{ij}^{el}(r) = z_i z_j e^2 / (4\pi\epsilon_0\epsilon_W r)$ is the Coulomb interaction energy between two ions i and j , and $h_{ij}(r)$ is the total correlation function which represents the excess probability that ions i and j are separated by a distance r . In Eq. (9), $h_{ij}(\sigma_{ij})$ designates this function at contact ($r = \sigma_{ij}$).

So, in Eq. (9), $\beta E^{DH}/V$ may be evaluated by using Eq. (10) with the DH correlation function,

$$h_{ij}^{DH}(r) = -z_i e \psi_j(r) / (k_B T) = -z_j e \psi_i(r) / (k_B T) \quad (11)$$

in which $\psi_i(r)$ is the mean electrostatic potential around ion i [1–4, 64].

2.3.1. Case of ions having the same size

The basic approach of Pitzer is recalled now. Details are given in Appendix C.

Pitzer assumed that all ions have the same distance of closest approach σ . In this case, the last term in Eq. (9), depending on the contact functions, $h_{ij}(\sigma)$, cancels out because of the electroneutrality condition, $\sum_i \rho_i z_i = 0$. Next, in order to obtain a better result from the virial equation (9), Pitzer suggested to include, in the expression of $h_{ij}(\sigma)$, an additional quadratic term in the electrostatic potential ψ_i at contact, namely

$$h_{ij}(\sigma) \simeq -z_j e \psi_i(\sigma) / (k_B T) + \frac{1}{2} \left[z_j e \psi_i(\sigma) / (k_B T) \right]^2 \quad (12)$$

By taking into account this quadratic term in ψ_i^2 at contact in the virial equation, he obtained an alternative expression for the osmotic coefficient. Then, by integration, the corresponding Helmholtz energy was determined. The expressions obtained by Pitzer [17, 41] in this case are recalled in Appendix C.

2.3.2. Case of ions of different sizes

Now, we present an extension of this approach in the case of ions of different diameters, which does not seem to have been proposed previously in the literature.

It is assumed that the DH distribution functions $h_{ij}^{DH}(r)$ are given by the DH formula in which the closest approach distance is $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, which gives,

$$h_{ij}^{DH}(r) = -\lambda \frac{z_i z_j}{(1 + \kappa \sigma_{ij}) r} e^{-\kappa(r - \sigma_{ij})} \quad (13)$$

Then using Eq. (10), the internal energy E^{DH} is given by

$$\beta E^{DH}/V = -2\pi \frac{\lambda^2}{\kappa} \sum_{j,k} \rho_j \rho_k \frac{z_j^2 z_k^2}{1 + \kappa \sigma_{jk}} \quad (14)$$

By following Pitzer's recipe, the osmotic coefficient is computed using the virial route,

$$\Phi^P = -\lambda \frac{2\pi}{3\rho_t} \sum_{j,k} \rho_j \rho_k \frac{z_j z_k}{1 + \kappa \sigma_{jk}} \left[\sigma_{jk}^2 + \frac{\lambda z_j z_k}{\kappa} \left(1 - \frac{1}{2} \frac{\kappa \sigma_{jk}}{1 + \kappa \sigma_{jk}} \right) \right] \quad (15)$$

By integration, the Helmholtz energy is deduced. It is found that

$$\beta A^P/V = \beta A^{(1)}/V + \beta A^{(2)}/V \quad (16)$$

with

$$\beta A^{(1)}/V = \frac{4\pi\lambda}{3\kappa^2} \sum_{j,k} \rho_j z_j \rho_k z_k [\ln(1 + \kappa \sigma_{jk}) - \kappa \sigma_{jk}] \quad (17)$$

and

$$\beta A^{(2)}/V = -\frac{2\pi\lambda^2}{3\kappa} \sum_{j,k} \rho_j z_j^2 \rho_k z_k^2 \frac{1}{\kappa \sigma_{jk}} \left[\ln(1 + \kappa \sigma_{jk}) + \frac{\kappa \sigma_{jk}}{1 + \kappa \sigma_{jk}} \right] \quad (18)$$

When all ions have the same diameter, the term $\beta A^{(2)}/V$ leads to the expression (C.8) obtained by Pitzer. The term $\beta A^{(1)}/V$ is nonzero only when the ions have different sizes. Next, the individual activity coefficients can be obtained by differentiation of $\beta A^{(1)}/V$ and $\beta A^{(2)}/V$ w.r.t. the number density of i . One gets,

$$\ln \gamma_i^P = \ln \gamma_i^{(1)} + \ln \gamma_i^{(2)} \quad (19)$$

where

$$\begin{aligned} \ln \gamma_i^{(1)} &= \frac{2}{3} \frac{z_i}{\mathcal{S}} \sum_j \rho_j z_j [\ln(1 + \kappa \sigma_{ij}) - \kappa \sigma_{ij}] \\ &\quad - \frac{z_i^2}{3\mathcal{S}^2} \sum_{j,k} \rho_j z_j \rho_k z_k \left[\ln(1 + \kappa \sigma_{jk}) - \kappa \sigma_{jk} + \frac{\kappa^2 \sigma_{jk}^2}{2(1 + \kappa \sigma_{jk})} \right] \end{aligned} \quad (20)$$

$$\begin{aligned} \ln \gamma_i^{(2)} = & -\frac{\kappa\lambda}{3\mathcal{S}} z_i^2 \sum_j \rho_j z_j^2 \frac{1}{\kappa\sigma_{ij}} \left[\ln(1 + \kappa\sigma_{ij}) + \frac{\kappa\sigma_{ij}}{1 + \kappa\sigma_{ij}} \right] \\ & + \frac{\kappa\lambda}{6\mathcal{S}^2} z_i^2 \sum_{j,k} \rho_j z_j^2 \rho_k z_k^2 \frac{1}{\kappa\sigma_{jk}} \left[\ln(1 + \kappa\sigma_{jk}) + \frac{\kappa^2\sigma_{jk}^2}{2(1 + \kappa\sigma_{jk})^2} \right] \end{aligned} \quad (21)$$

with

$$\mathcal{S} = \sum_k \rho_k z_k^2 \quad (22)$$

2.4. The MSA

The theory underlying the MSA for primitive electrolytes has been explained in detail in the literature [26, 73, 74]. The main equations are given in Appendix D.

Less classic formulas are given now for the single ion activity coefficients.

2.4.1. Single ion activity coefficients in the MSA

Valuable expressions have been derived quite recently for this quantity. Gillespie et al. [75] found that the individual activity coefficients $\ln \gamma_i$ obtained from MC calculations are not well described when using the classic MSA formulas [54] obtained by this differentiation. Then, a semi-empirical correction was introduced by these authors in the MSA, that allowed them to better reproduce the MC results. This new theory was named the Mean Countershell Approximation (MCSA).

Subsequently, it was shown in 2022 in a rigorous (not empirical) manner [76] that the classic expression for the individual activity coefficient of an ion i within the MSA should be corrected as follows,

$$\ln \gamma_i^{MSA} = \ln \gamma_i^{MSA,0} + 2z_i\beta u^* \quad (23)$$

in which the first part on the r.h.s. is the classical contribution [54] given by,

$$\ln \gamma_i^{MSA,0} = -\lambda \left[\frac{\Gamma z_i^2}{1 + \Gamma\sigma_i} + \eta\sigma_i \left(\frac{2z_i - \eta\sigma_i^2}{1 + \Gamma\sigma_i} + \frac{\eta\sigma_i^2}{3} \right) \right] \quad (24)$$

and the second part is the corrective extra term in which,

$$\beta u^* = -\frac{\pi\lambda}{6} \sum_k \rho_k \sigma_k^2 \left(N_k \sigma_k + \frac{3}{2} z_k \right) \quad (25)$$

with,

$$N_k = -\frac{\Gamma z_k + \eta\sigma_k}{1 + \Gamma\sigma_k} \quad (26)$$

The additional contribution, proportional to z_i , in Eq. (23) had been mentioned previously [77] (but it was not demonstrated there).

In Refs. 76 and 78, it was found that the corrected MSA expressions [Eqs. (23)-(26)], like those of MCSA, much better describe individual activity coefficients found in MC simulations.

The electrostatic contribution to the mean salt activity coefficient is obtained by averaging the individual contributions, $\ln \gamma_i^{MSA}$ according to Eq. (4). Then, it is noted that the contribution proportional to z_i in Eq. (23) vanishes in the expression of γ_S because of the electroneutrality condition, $\sum \rho_i z_i = 0$. The equation given previously in Refs. 26, 54, 74 is then recovered.

2.4.2. Virial route for the MSA

In view of the method proposed by Pitzer, expounded in Section 2.3, one may wonder whether the virial route could also be employed with the MSA total correlation functions. This method is now investigated.

When the ions all have the same diameter, the osmotic coefficient can also be computed from Eq. (9), following Pitzer's recipe. To this end, we first look at the terms depending on the contact correlation functions. In the MSA theory the functions $h_{ij}(\sigma)$ at contact are given by

$$h_{ij}^{MSA}(\sigma) = h_{ij}^{HS}(\sigma) - \lambda \frac{z_i z_j}{\sigma (1 + \Gamma \sigma)^2} \quad (27)$$

The first term $h_{ij}^{HS}(\sigma)$, is the hard sphere contribution which has been studied previously for neutral hard spheres and is left aside here in this calculation of the electrostatic contribution to the osmotic coefficient.

We note that the electrostatic contribution to $h_{ij}^{MSA}(\sigma)$, proportional to $z_i z_j$, is very similar to the corresponding one in the DH theory given by Eq. (C.3). Then, as in the DH theory, the term depending on these functions $h_{ij}(\sigma)$ in the virial equation makes a zero contribution to Φ_{virial} because of electroneutrality. Next, if, as suggested by Pitzer, a quadratic term is added in the definition of the distribution function at contact

$$h_{ij}(\sigma) \simeq h_{ij}^{MSA}(\sigma) + \frac{1}{2} \left[\frac{z_i z_j \lambda}{\sigma (1 + \Gamma \sigma)^2} \right]^2 \quad (28)$$

starting from Eq. (9) we get

$$\Phi_{virial}^{MSA} = \frac{\beta E^{MSA}/V}{3\rho_t} + \frac{\Gamma^4 \sigma}{3\pi \rho_t} \quad (29)$$

Next, the internal energy can be evaluated, which leads to

$$\begin{aligned} \frac{\beta E^{MSA}/V}{3\rho_t} &= -\frac{\lambda \Gamma}{3\rho_t(1 + \Gamma \sigma)} \sum_i \rho_i z_i^2 \\ &= -\frac{\Gamma^3}{3\pi \rho_t} (1 + \Gamma \sigma) \end{aligned} \quad (30)$$

By substituting this result in the previous equation we arrive at

$$\Phi_{virial}^{MSA} = -\frac{\Gamma^3}{3\pi \rho_t} \quad (31)$$

Thus, Eq. (D.6), obtained by differentiation of the Helmholtz energy, is recovered through the virial route. This somewhat surprising result is likely a consequence of a better consideration of excluded volume effects on the deviations from ideality in the MSA.

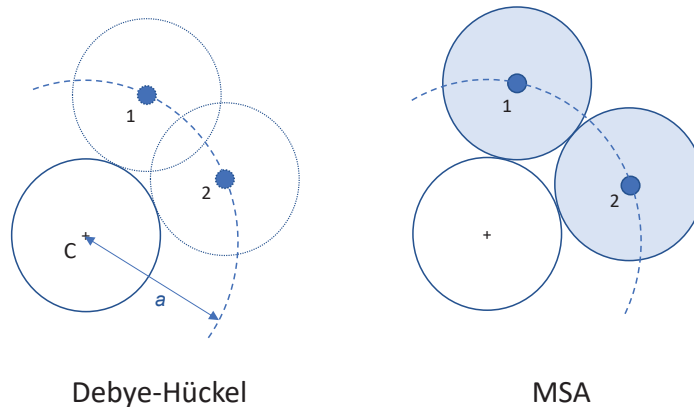


Figure 1: Volume exclusion in DH and MSA theories. In DH, there is a minimum distance a between the central ion C and ions in the cloud. However, the latter ions may overlap because they are taken as point particles in DH. In the MSA, volume exclusion prevails consistently for all ions.

2.5. Main difference between DH and MSA theories

In DH theory, ions are modeled as point charges with a minimum separation distance [6]. However, some caution has to be exercised about the precise meaning of this statement. It may deserve some comments as follows.

The situation is illustrated in Figure 1.

In the DH approximation, the ions cannot approach the central ion to a distance that is less than some minimum distance. However, ions *in the cloud* are treated in a different manner. They are regarded as point charges, without a minimum distance of approach between them. There is *no* restriction on their separation distance. If there was such an exclusion condition also in the cloud, then the Boltzmann distribution involved in the DH demonstration would be different; it would have to take this exclusion into account, which it does not. Introducing this condition in the treatment would highly complicate it and, if the problem could be solved, it would likely lead to a result similar to the MSA. It is noted that the fact that ions in the ionic atmosphere are taken as point charges, with no volume exclusion, was not explicitly specified in the original work by Debye and Hückel (but they clearly used this assumption in their treatment).

In contrast with DH assumptions, the MSA treats excluded volume between ions in a consistent way, on the same footing for all ions. Being the result of the solution to an Ornstein-Zernike for all ionic species, it does not single out one ion in particular (the central ion), it treats the system of ions as a whole.

As a consequence, since introducing the excluded volume of ions in the cloud in DH model will expand the system, it ensues that the characteristic screening length in the MSA is larger than in DH, that is one must have $1/(2\Gamma) > 1/\kappa$, or $\Gamma < \kappa/2$, which relation may be checked by using Eq. (D.4).

3. Results and discussion

The results obtained from the various theories reviewed in the preceding section were compared with those found using Monte-Carlo simulations, carried out by Abbas et al. [47] (data reported in the Supporting Information addendum) and by Gutierrez et al. [48]. Values for the mean activity and osmotic coefficients were reported in these references. In Ref. 48 the results were compared with data obtained using the HNC theory, which is expected to be of higher accuracy than the MSA. Moreover, *individual* activity coefficients of cation and anion were computed in Ref. 47.

A few systems were selected from these two references. The conditions for which the MC method was employed are summarized in Table 1. The systems were chosen among a large number for the significant size asymmetry of the cation and anion, which results in quite different individual activity coefficients of cation and anion. Only in the last system do the ions have equal diameters.

Table 1: Values of parameters used in the MC studies (subscripts + and - indicate cation and anion, respectively).

σ_+ (Å)	σ_- (Å)	z_+	z_-	λ (Å)	Ref.
1.38	3.08	1	-1	7.150 ^a	47 ^b
5.90	3.62	2	-1	7.150	47 ^c
6.20	3.82	3	-1	7.150	47 ^d
4.25	4.25	2	-2	7.14	48 ^e

^aWith $T = 298$ K and $\epsilon_W = 78.4$; ^bSystem S75; ^cSystem S38; ^dSystem S104; ^eTable 5.

3.1. Mean salt activity and osmotic coefficients

Firstly, mean activity and osmotic coefficients from MC calculations are compared with the results from DH, Pitzer, MSA, and HNC (in the case of a 2-2 salt [48]) theories. The results are shown in Figures 2-5.

In the left panel of Figure 2, $\ln(\gamma_S)$ is plotted against \sqrt{C} , showing that all theories obey the Debye-Hückel limiting law (in \sqrt{C}) at very low concentration.

More results are presented in the Supplementary Material addendum in the case of 1-1 and 2-1 salts with equisized cation and anion.

The results for the mean salt activity coefficient, γ_S , in these figures show that the performance of the theories to describe the MC data are in the following order: MSA > Pitzer > DH. As regards the osmotic coefficient, MSA and Pitzer models overall perform comparably. It is to be noted that, for a 1-1 salt with equisized cation and anion, the result from DH and Pitzer is significantly less good than from MSA when the diameter of the ions is decreased, as may be observed in Figures S4 and S5.

In the case of the 1-1 salt (Figure 2) and of the 2-2 salt (Figure 5), the result from Pitzer gives results that are closer to the MC data at moderate concentration, while the MSA yields relatively better agreement

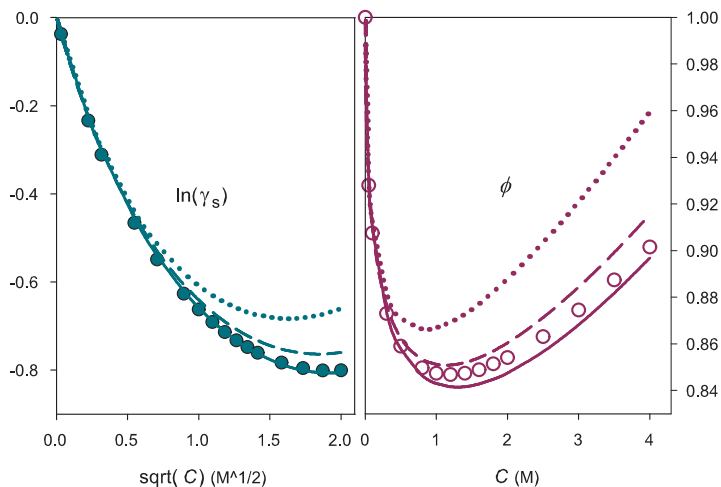


Figure 2: Mean salt activity ($\ln(\gamma_S)$, left panel) and osmotic (right) coefficients for a 1-1 electrolyte with $\sigma_+ = 1.38 \text{ \AA}$ and $\sigma_- = 3.08 \text{ \AA}$. Symbols: MC data from Ref. 47 (system S75); Solid lines: MSA; Dashed lines: Pitzer; Dotted lines: DH.

at higher concentration. In these two cases where the size asymmetry is large (first case) or the valence of the ions is high (second case), respectively, the performance of DH theory is notably poor.

It is noticed in the case of multivalent electrolytes (2-1, 3-1 and 2-2 salts) that the mean activity coefficients are larger than the MC data, and that the deviation increases with concentration. This behavior may be attributed to the fact that the MSA (like the DH approximation) is a linearized theory that fails to fully describe the effect of strong electrostatic interactions, especially at short interionic separations. As a consequence, the MSA accounts partly for these attractive interactions, which results in mean salt activity coefficients being a little too high as compared to the ‘exact’ MC value. Because the HNC theory is not a linearized theory, it is able to better handle the effect of electrostatic forces in multivalent electrolytes. This can be seen for the γ_S in Figure 5 in which HNC gives the best agreement with MC data. Nevertheless, the HNC osmotic coefficient is somewhat less good at the highest concentrations in this same figure.

The relative weakness of the MSA in the case of multivalent electrolytes has been corrected in the literature by introducing association of unlike ions in order to add some extra attraction between these ions [55, 79].

3.2. Individual ion activity coefficients

Individual activity coefficients of cation and anion reported in Ref. 47 were compared with MSA and Pitzer results. There are no results from the DH theory here because it uses the mean cation-anion size for the closest approach distance (not individual sizes), and for the data relative to the 2-2 salt from Ref. 48 in which the cation and anion had the same diameter.

The results are shown in Figures 6-8. Note that a log scale is used for convenience for the activity

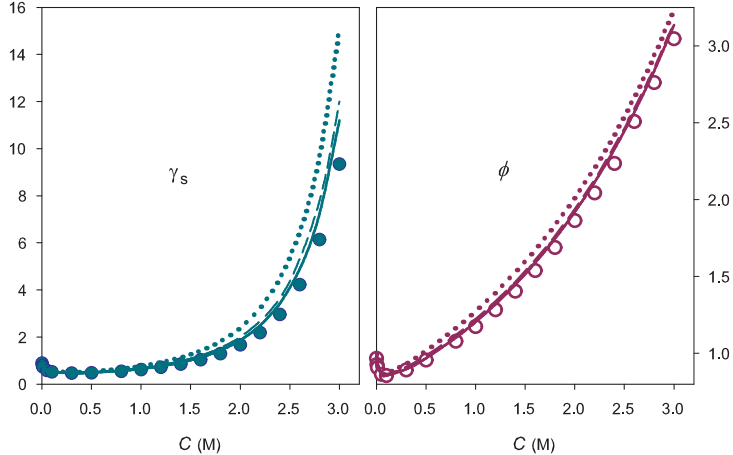


Figure 3: Mean salt activity (left) and osmotic (right) coefficients for a 2-1 electrolyte with $\sigma_+ = 5.90 \text{ \AA}$ and $\sigma_- = 3.62 \text{ \AA}$. Symbols: MC data from Ref. 47 (system S38); Solid lines: MSA; Dashed lines: Pitzer; Dotted lines: DH. The Pitzer result for Φ cannot be distinguished from the MSA.

coefficients in the last two figures.

In the 3 cases shown here, it is seen that the MSA gives better results than those derived in this work from Pitzer’s approach, except for the anion at high concentration in Figure 8. The MSA activity coefficient of cation is below the MC in Figure 6 where the cation is smaller than the anion (system S75), and it is located above in the other two systems (Figures 7 and 8). In contrast, the MSA result of the anion is above the MC in the 3 cases.

It was noticed that the corrective term, $2z_i\beta u^*$, in Eq. (23) makes a significant contribution to $\ln \gamma_i^{MSA}$. It is for example of the order of $\sim 20\%$ in the case of the two ions of the 1-1 salt (system S75), and of $\sim 30\text{-}35\%$ for those of the 3-1 salt (system S104). The relative deviations of γ_+ and γ_- from the MC data at the highest concentrations are -4.4% and 3.5% in Figure 6 (1-1 salt), 26% and 17% in Figure 7 (2-1 salt), and 80% and 25% in Figure 8 (3-1 salt). In the latter system, the MC value for γ_+ goes as low as ~ 0.007 , which indicates very strong electrostatic interactions for this trivalent cation with its environment. Recovering accurately such a small value with a model like the ones presented here is therefore quite challenging.

The Pitzer values of the cation activity coefficient are close to the MSA ones in the case of the 1-1 salt. This is not so in the case of the other two systems (the 2-1 and 3-1 salts), where the Pitzer result deviates notably from the MC values. The reverse is true in the case of the anion activity coefficients. It is also seen in Figures 7 and 8 that, unlike the MSA, the Pitzer values are below the MC points.

It is moreover observed that the MSA performs increasingly better than Pitzer in the case of the cation when its valence increases. However, at the same time, the MSA result for the cation deviates more and more from the MC values when its valence is risen from $+1$ to $+3$. This increasing deviation may again be

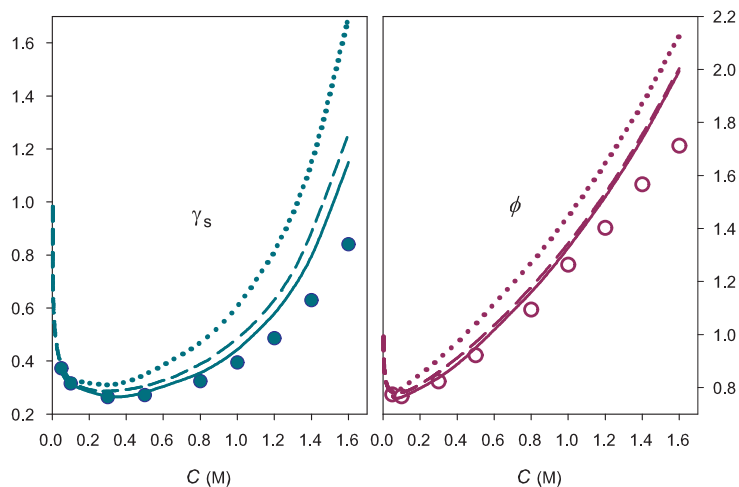


Figure 4: Mean salt activity (left) and osmotic (right) coefficients for a 3-1 electrolyte with $\sigma_+ = 6.2 \text{ \AA}$ and $\sigma_- = 3.82 \text{ \AA}$. The osmotic coefficient from Pitzer’s treatment is just above the MSA. Symbols: MC data from Ref. 47 (system S104); Solid lines: MSA; Dashed lines: Pitzer; Dotted lines: DH.

caused by the MSA becoming less accurate because the linearization involved in this theory becomes less and less capable of handling the strong electrostatic field in the vicinity of the cation. On the other hand, the MSA values for the anions are comparatively more accurate (closer to the MC) than for the cations, likely because their valence is of -1 in the 3 cases. We also note that they are slightly less accurate than the Pitzer results in the case of the 3-1 salt at the highest concentrations.

Possible explanations for the respective behaviors of MSA and Pitzer activity coefficients for cation and anion are not at hand yet. This point could be the subject of future investigation.

Nevertheless, to summarize, it may be said from these results that the MSA provides very reasonable estimates for the individual activity coefficients. It would be interesting to examine in the future the case of a 2-2 salt for which no MC data seem to be available presently.

3.3. Fit of MC mean salt activity coefficients

In Ref. 6 it was found that results from the DH model could be fitted to those from the MSA up to a concentration of 5M by using a mean ion size that would be of the order of $5/6$ ($\simeq 0.83$) the original size. The correcting factor depends slightly on the ion diameter, and on the maximum salt concentration to which comparison is made.

In the present work, the DH and MSA mean salt activity coefficients were fitted to the MC values by modifying in equal proportions the diameters of cation and anion listed in Table 1. These adjustments were done on the full activity coefficient, and also on the electrostatic parts (superscript *el*). The latter MC values were obtained by subtracting the HS contributions from the raw MC data, that is by using the following

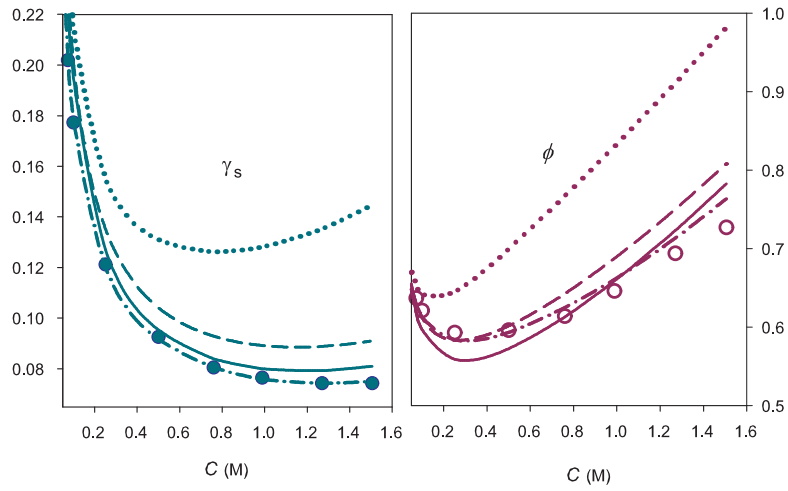


Figure 5: Mean salt activity (left) and osmotic (right) coefficients for a 2-2 electrolyte with $\sigma_+ = \sigma_- = 4.25 \text{ \AA}$ for concentrations above 0.1 M (for convenience). Symbols: MC data from Ref. 48; Solid lines: MSA; Dashed lines: Pitzer; Dotted lines: DH; Dash-dotted lines: HNC [48].

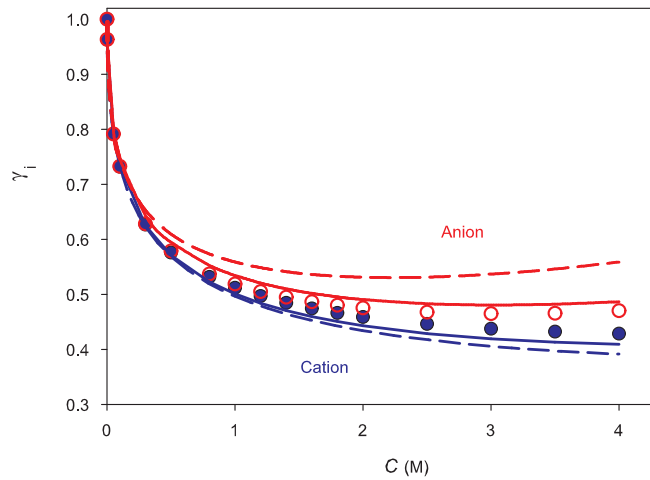


Figure 6: Individual activity coefficients for the 1-1 electrolyte of Figure 2 ($\sigma_+ = 1.38 \text{ \AA}$ and $\sigma_- = 3.08 \text{ \AA}$). Symbols: MC data from Ref. [47]; Solid lines: MSA; Dashed lines: Pitzer.

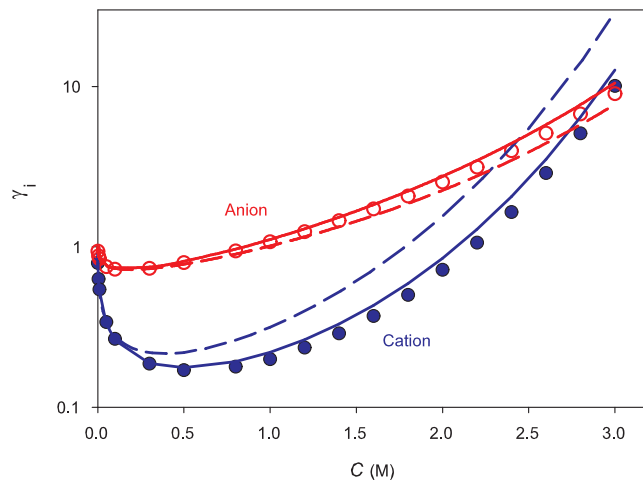


Figure 7: Individual activity coefficients for the 2-1 electrolyte of Figure 3 ($\sigma_+ = 5.90 \text{ \AA}$ and $\sigma_- = 3.62 \text{ \AA}$). Symbols: MC data from Ref. 47; Solid lines: MSA; Dashed lines: Pitzer.

formula,

$$\ln \gamma_{MC}^{el} = \ln \gamma_{MC} - \ln \gamma^{HS} \quad (32)$$

in which subscript S is omitted for clarity and the HS part was estimated using Eq. (A.2). In the fits, the sum of the squares of the relative deviations was minimized (objective function).

A plot of the HS and electrostatic contributions, $\ln \gamma^{HS}$ and $\ln \gamma_{MC}^{el}$ found from Eq. (32), is shown in Figures 9 and 10 for the 1-1 and 2-2 salts, respectively.

The results of the fits are presented in Table 2 where α stands for the single optimum multiplicative factor applied to the two ion diameters σ_i used in the MC simulations: $\sigma'_i = \alpha \sigma_i$, and σ'_i is used to compute DH and MSA values for γ_S . The best values of α_{DH}^{HS+el} (for a fit of the full ‘HS+el’ γ_S^{DH}) and α_{DH}^{el} (for a fit of the electrostatic part of γ_S^{DH}), and similarly α_{MSA}^{HS+el} and α_{MSA}^{el} , were determined for the systems considered in Table 1. The table contains the AARD’s of fit where AARD represents the average absolute relative deviation for the simulation points reported in Refs. 47 and 48.

These results indicate that the ion sizes have to be reduced in order to enhance attractive forces between unlike ions. The shrinkage needs to be larger with DH model than with the MSA. Deviations of fit increase noticeably in the case of multivalent ions. AARD’s of fit are generally appreciably higher with DH model than with MSA, except in the case of the 2-2 salt. The fits of the raw (HS + el) MC mean salt activity coefficients generally lead to lower AARD values than in the fits of the electrostatic part, and the corresponding values for α are closer to unity.

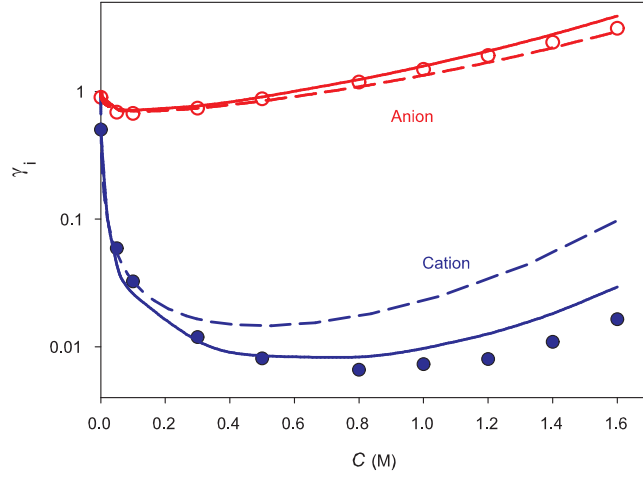


Figure 8: Individual activity coefficients for the 3-1 electrolyte of Figure 4 ($\sigma_+ = 6.2 \text{ \AA}$ and $\sigma_- = 3.82 \text{ \AA}$). Symbols: MC data from Ref. 47; Solid lines: MSA; Dashed lines: Pitzer.

Table 2: Results for the fits of MC values for γ_S by using modified ion diameters in DH and MSA models ($\sigma'_i = \alpha \sigma_i$). The AARD's of fit are given in brackets below α values.

z_+	z_-	α_{DH}^{HS+el}	α_{MSA}^{HS+el}	α_{DH}^{el}	α_{MSA}^{el}
1	-1	0.898 (0.4 %)	1.002 (0.5 %)	0.805 (0.6 %)	1.002 (0.5 %)
2	-1	0.968 (6.5 %)	0.990 (1.4 %)	0.709 (4.7 %)	0.889 (2.3 %)
3	-1	0.927 (2.8 %)	0.975 (2.1 %)	0.728 (10.2 %)	0.891 (6.2 %)
2	-2	0.835 (4.8 %)	0.978 (6.3 %)	0.758 (5.3 %)	0.958 (6.1 %)

4. Conclusion

The DH paper of 1923 was a scientific landmark paving the way for the advent of many other theories dedicated to electrolyte solutions.

The present study shows that the DH theory is now superseded by other analytical models like Pitzer's treatment and the MSA. Their accuracy to describe results from Monte-Carlo simulations is significantly higher. However, it is also clear that, in the case of a binary salt solution, the DH closest approach distance may be adjusted so as to recover the results of more accurate theories as suggested elsewhere [6].

Nevertheless, this suggestion was arrived at by considering moderately concentrated binary solutions. The obtainment of satisfactory results in the case of mixtures, and at higher concentrations, has not been

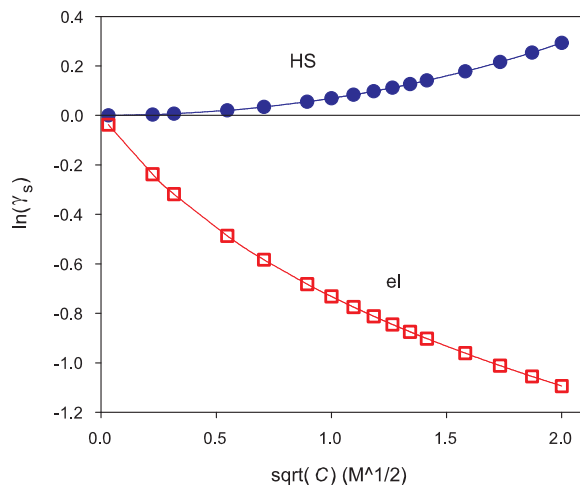


Figure 9: HS and electrostatic contributions, $\ln \gamma^{HS}$ and $\ln \gamma_{MC}^{el}$, against \sqrt{C} for the 1-1 electrolyte of Figure 2 ($\sigma_+ = 1.38 \text{ \AA}$ and $\sigma_- = 3.08 \text{ \AA}$). MC data from Ref. 47; Upper line: HS; Bottom line: electrostatic.

evaluated yet.

In the case of a single salt solution, the DH treatment does not allow one to estimate individual ion activity coefficients as the MSA and Pitzer equations do. It can only provide mean salt activity coefficients in that case because the minimum distances of approach are equal for the two ions. Nevertheless, the DH approach remains a fruitful source of inspiration for describing electrostatic interactions between ions. As an example, the expressions of Pitzer's theory are deduced from the total correlation functions issued by the DH theory.

According to the present study for strong salts, the accuracy of the Pitzer formula for the mean salt activity and osmotic coefficients seems nearly comparable to that of the MSA. The MSA, which better accounts for the sizes of the ions, gives more accurate results than other analytical theories. Like the Pitzer model, it applies only to strong salts. It does not account for association (electrostatic ion-pairing or chemical bonding).

Nevertheless, the associative MSA [79, 80] and Binding-MSA (BiMSA) [39, 81, 82] could describe such systems. The introduction of association in the MSA would produce a better agreement between the theoretical and simulation results, in particular in the case of the 2-2 electrolytes in water probably, or of lower valence electrolytes in solvents of low dielectric constant. Moreover, when the electrostatic and excluded volume interactions are properly taken into account, the added associative contributions may be used to model the influence of specific interactions.

In a subsequent study, we will examine the case of electrolyte mixtures with common anion. In this type of solution, it will be possible to ascribe values to the minimum distances of approach for all ions in the

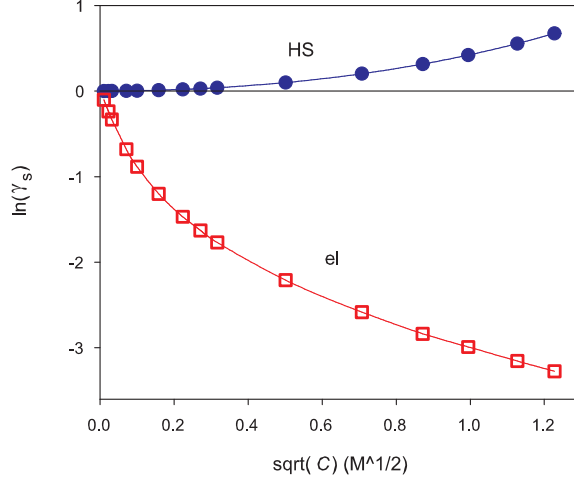


Figure 10: Individual activity coefficients for the 2-2 electrolyte of Figure (5) ($\sigma_+ = \sigma_- = 4.25 \text{ \AA}$). Symbols: MC data from Ref. 48; Upper line: HS; Bottom line: electrostatic.

DH theory. Dealing with complex mixtures involving various types of cations and anions would be more problematic on this point. Maybe this case would deserve being studied with more attention in the future.

It may also be interesting to obtain more MC results, such as for instance the values of individual activity coefficients in solutions of 2-2 salts.

Supplementary Material: More results in the case of 1-1 and 2-1 salts with equisized cation and anion.

Appendix A. Excluded volume contribution

For comparison with Monte-Carlo simulation data, it is required to add up a contribution arising from the volume excluded by the ions, as expressed by Eq. (3). This contribution is needed for analytical theories with implicit solvent, that is in particular for DH (although it is sometimes not used [52]), Pitzer and MSA, except in very dilute solutions where electrostatic interactions are dominant.

Here the same HS contribution was added to DH, Pitzer and MSA expressions, for the activity and osmotic coefficients. The Mansoori-Carnahan-Starling-Leland equations for this part are very accurate [58].

$$\ln \gamma_i^{HS} = -\ln \Delta + \sigma_i F_1 + \sigma_i^2 F_2 + \sigma_i^3 F_3 \quad (\text{A.1})$$

in which F_1 , F_2 and F_3 are given by [54],

$$F_1 = \frac{3X_2}{\Delta}, \quad F_2 = \frac{3X_1}{\Delta} + 3\frac{X_2^2}{X_3} \frac{1}{\Delta^2} + 3\frac{X_2^2}{X_3^2} \ln \Delta$$

$$F_3 = \left(X_0 - \frac{X_2^3}{X_3^2} \right) \frac{1}{\Delta} + \frac{3X_1X_2 - X_2^3/X_3^2}{\Delta^2} + 2\frac{X_2^3}{X_3} \frac{1}{\Delta^3} - 2\frac{X_2^3}{X_3^3} \ln \Delta$$

where

$$X_n = \frac{\pi}{6} \sum_k \rho_k \sigma_k^n$$

By virtue of Eqs. (4) and (A.1) one gets the mean salt HS activity coefficient,

$$\ln \gamma_S^{HS} = \left(\frac{X_2^3}{X_0 X_3^2} - 1 \right) \ln \Delta + \frac{X_3}{\Delta} + \frac{3X_1X_2(2 - X_3)}{X_0 \Delta^2} + \frac{X_2^3(1 + 2X_3 - X_3^2)}{X_0 X_3 \Delta^3} \quad (\text{A.2})$$

after correction of a misprint in Eq. (34) of Ref. 54, in the denominator of the second-last term (Δ^3 instead of Δ^2).

The equation for the hard sphere contribution to the osmotic coefficient is [54, 58],

$$\Phi^{HS} = \frac{X_3}{\Delta} + 3\frac{X_1X_2}{X_0 \Delta^2} + X_2^3 \frac{3 - X_3}{X_0 \Delta^3} \quad (\text{A.3})$$

For equisized hard spheres, the equation for the activity coefficient simplifies as [83],

$$\ln \gamma_i^{HS} = X_3 \frac{8 - 9X_3 + 3X_3^2}{\Delta^3} \quad (\text{A.4})$$

Appendix B. Basic formulas from DH theory

The result for the Helmholtz energy A^{DH} for an arbitrary system of ions may be written as,

$$\beta A^{DH}/V = -\lambda \frac{1}{\kappa^2} \sum_i \frac{\rho_i z_i^2}{a_i^3} f(x_i) \quad (\text{B.1})$$

where V is the volume of solution,

$$f(x) = \ln(1+x) - x + \frac{1}{2}x^2 \quad (\text{B.2})$$

and

$$x_i = \kappa a_i \quad (\text{B.3})$$

where a_i is the minimum distance of approach to ion i .

The activity coefficient of an ion i obtained by differentiation of $\beta A^{DH}/V$ [Eq. (B.1)] w.r.t. ρ_i is,

$$\ln \gamma_i^{DH} = -\lambda z_i \left[\frac{1}{\kappa^2 a_i^3} f(x_i) + 4\pi \lambda \frac{1}{\kappa^4} \sum_j \frac{\rho_j z_j^2}{a_j^3} g(x_j) \right] \quad (\text{B.4})$$

with

$$g(x) = -f(x) + \frac{1}{2} \frac{x^3}{1+x} = -\ln(1+x) + \frac{1}{2} \frac{x(2+x)}{1+x} \quad (\text{B.5})$$

The DH contribution to the mean activity coefficient of an electrolyte is evaluated according to Eq. (4). So, one obtains using Eq. (8) and after some simplifications,

$$\ln \gamma_S^{DH} = -\frac{\lambda}{2} \frac{\kappa}{\rho_t} \sum_i \frac{\rho_i z_i^2}{1 + \kappa a_i} \quad (\text{B.6})$$

The contribution from electrostatic interactions to the osmotic coefficient can be found from the general relation (6), which yields,

$$\Phi^{DH} = -\frac{\lambda\kappa}{\rho_t} \sum_i \rho_i z_i^2 \left[\frac{1}{2(1+x_i)} - \frac{1}{x_i^3} f(x_i) \right] \quad (\text{B.7})$$

It was verified that, in the limit of infinite dilution ($\kappa \rightarrow 0$), Eqs. (B.4) and (B.7) give the correct limiting laws,

$$\ln \gamma_i^{DH} \sim -\lambda \frac{\kappa}{2} z_i^2, \quad \Phi^{DH} \sim -\frac{\kappa^3}{24\pi\rho_t} \quad (\text{B.8})$$

When all ions are ascribed the same minimum distances of approach, $a_i = a$, then Eqs. (B.1), (B.4), (B.6), and (B.7) simplify to,

$$\beta A^{DH}/V = -\frac{1}{4\pi a^3} f(x) \quad (\text{B.9})$$

with $x = \kappa a$,

$$\ln \gamma_i^{DH} = -\frac{\lambda}{2} \frac{\kappa}{1+\kappa a} z_i^2, \quad \ln \gamma_S^{DH} = -\frac{1}{8\pi\rho_t} \frac{\kappa^3}{1+\kappa a} \quad (\text{B.10})$$

$$\Phi^{DH} = -\frac{\kappa^3}{8\pi\rho_t} \left[\frac{1}{1+x} - 2 \frac{f(x)}{x^3} \right] \quad (\text{B.11})$$

Appendix C. Pitzer's approach

In this section, the method employed by Pitzer in the case all ions have the same distance of closest approach is recalled. This common distance is hereafter denoted as σ .

In DH theory, the potential $\psi_j(r)$ is given by,

$$\psi_j(r) = \frac{z_j e}{4\pi\epsilon_0\epsilon_W(1+\kappa\sigma)r} e^{-\kappa(r-\sigma)} \quad (\text{C.1})$$

By virtue of Eqs. (10) and (11), one gets,

$$\begin{aligned} \beta E^{DH}/V &= 2\pi\lambda \sum_{i,j} \rho_i z_i \rho_j z_j \int_{\sigma}^{\infty} h_{ij}^{DH}(r) r dr \\ &= \frac{-\kappa^3}{8\pi(1+\kappa\sigma)} \end{aligned} \quad (\text{C.2})$$

The DH total pair correlation function at contact stems from Eqs. (11) and (C.1) as,

$$h_{ij}^{DH}(\sigma) = -\lambda \frac{z_i z_j}{\sigma(1+\kappa\sigma)} \quad (\text{C.3})$$

Because of the latter relation and the electroneutrality condition, $\sum_i \rho_i z_i = 0$, the last term in Eq. (9) cancels out. So we get,

$$\Phi_{virial}^{DH} = \frac{\beta E^{DH}/V}{3\rho_t} = \frac{-\kappa^3}{24\pi\rho_t(1+\kappa\sigma)} \quad (\text{C.4})$$

which is different than the result obtained by differentiation of the Helmholtz energy. This difference is a consequence of the approximations made to obtain analytical expressions in DH theory. In particular, the

fact that the term depending on the contact functions $h_{ij}(\sigma)$ leads to a zero contribution is a consequence of the linearization of the distribution functions in DH. Next, in order to obtain a better result from the virial equation, Pitzer suggested to include, in the expression of $h_{ij}(\sigma)$, an additional quadratic term in the electrostatic potential ψ_i at contact, namely

$$h_{ij}(\sigma) \simeq -z_j e \psi_i(\sigma) / (k_B T) + \frac{1}{2} \left[z_j e \psi_i(\sigma) / (k_B T) \right]^2 \quad (\text{C.5})$$

Then, by taking into account the quadratic term in ψ_i^2 at contact in the virial equation, Pitzer obtained the following more effective expression,

$$\Phi^P = \frac{-\kappa^3}{24\pi \rho_t (1 + \kappa\sigma)} + \frac{\kappa^4 \sigma}{48\pi \rho_t (1 + \kappa\sigma)^2} \quad (\text{C.6})$$

where the superscript ‘P’ denotes Pitzer’s corrections to the DH equations. Using

$$\frac{\beta A^P}{\rho_t} = \int \frac{\Phi^P}{\rho_t} d\rho_t \quad (\text{C.7})$$

Pitzer found,

$$\beta A^P / V = -\frac{\kappa^2}{24\pi \sigma} \left[\ln(1 + \kappa\sigma) + \frac{\kappa\sigma}{1 + \kappa\sigma} \right] \quad (\text{C.8})$$

Appendix D. Basic formulas from MSA theory

As in DH theory, the mean salt activity and osmotic coefficients may be obtained by differentiation of the Helmholtz energy A^{MSA} [74],

$$\beta A^{MSA} / V = \beta E^{MSA} / V + \frac{\Gamma^3}{3\pi} \quad (\text{D.1})$$

In Eq. (24) one has,

$$\eta = \frac{1}{\Omega} \frac{\pi}{2\Delta} \sum_k \frac{\rho_k \sigma_k z_k}{1 + \Gamma \sigma_k}, \quad \Omega = 1 + \frac{\pi}{2\Delta} \sum_k \frac{\rho_k \sigma_k^3}{1 + \Gamma \sigma_k} \quad (\text{D.2})$$

where $\beta = 1/k_B T$ (with T the temperature and k_B the Boltzmann constant), e is elementary charge, ε_0 is the permittivity of a vacuum, and $\Delta = 1 - \frac{\pi}{6} \sum_k \rho_k \sigma_k^3$ is the volume fraction of free space (not occupied by solute particles).

In the above equations, Γ is the MSA screening parameter which satisfies the equation,

$$\Gamma^2 = \pi \lambda \sum_k \rho_k \left[(z_k - \eta \sigma_k^2) / (1 + \Gamma \sigma_k) \right]^2 \quad (\text{D.3})$$

Its value can be easily determined numerically by rewriting Eq. (D.3) as $\Gamma = f(\Gamma)$ and using the iterative procedure $\Gamma_{n+1} = f(\Gamma_n)$ with, e.g., $\Gamma_0 = \kappa/2$, which converges in a few steps.

When all ions have the same diameter σ (restricted case), then $\eta = 0$ and Eqs. (23) and (D.3) simplify to give [54],

$$\Gamma = \left[(1 + 2\kappa\sigma)^{1/2} - 1 \right] / (2\sigma) \quad (\text{D.4})$$

$$\ln \gamma_i^{MSA} = -\lambda z_i^2 \frac{\Gamma}{1 + \Gamma\sigma} \quad (\text{D.5})$$

because in that case one has $u^* = 0$ in Eq. (25) as a consequence of the electroneutrality condition, $\sum \rho_i z_i = 0$.

In the restricted case, the electrostatic contribution to the osmotic coefficient is [74]

$$\phi^{MSA} = -\frac{\Gamma^3}{3\pi\rho_t} \quad (\text{D.6})$$

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Supplementary Material to paper
‘Insight into the ionic atmosphere effect:
Comparison of theories for electrolytes at the primitive level’

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Further results are given in this addendum.

First, Figures 2-4 are reproduced below, with the additional inclusion of experimental data corresponding to the salts treated by Abbas et al. [1]. Optimum average ion diameters were determined by fits of the MC simulation results.

In the figures below, the MC data (and the calculated curves) may deviate appreciably from the experimental data at the highest concentrations because the ion sizes were adjusted up to salt concentrations of the order of 1 M for the salts of Figures S1-S3, and 0.5 M for those of Figures S4-S7.

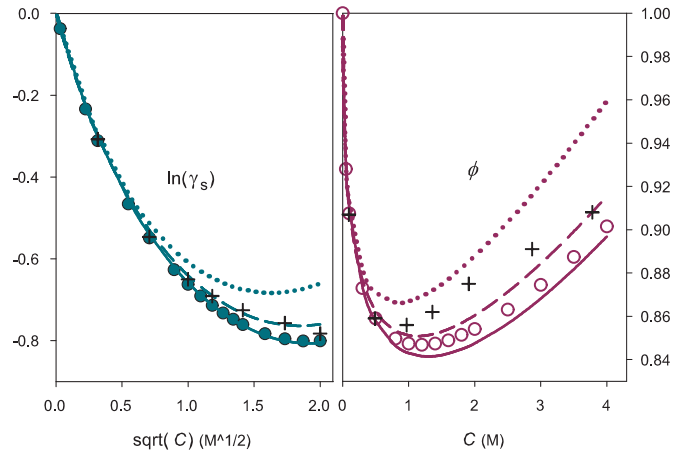


Figure S1: Mean salt activity ($\ln(\gamma_s)$, left panel) and osmotic (right) coefficients for a 1-1 electrolyte with $\sigma_+ = 1.38 \text{ \AA}$ and $\sigma_- = 3.08 \text{ \AA}$. Circles: MC data from Ref. 1 (system S75); Crosses: experimental data for LiOH aqueous solution [2]; Solid lines: MSA; Dashed lines: Pitzer; Dotted lines: DH.

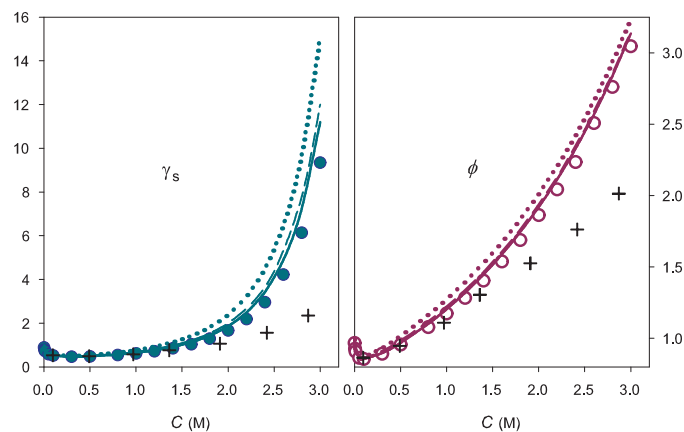


Figure S2: Mean salt activity (left) and osmotic (right) coefficients for a 2-1 electrolyte with $\sigma_+ = 5.90$ Å and $\sigma_- = 3.62$ Å. Circles: MC data from Ref. 1 (system S38); Crosses: experimental data for MgCl_2 aqueous solution [3]; Solid lines: MSA; Dashed lines: Pitzer; Dotted lines: DH. The Pitzer result for Φ cannot be distinguished from the MSA.

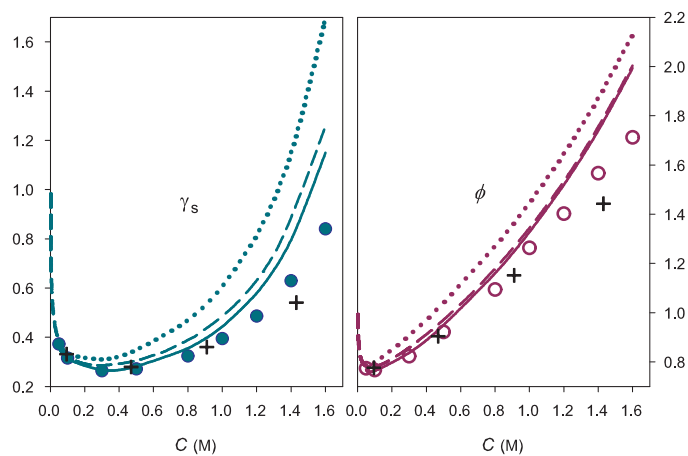


Figure S3: Mean salt activity (left) and osmotic (right) coefficients for a 3-1 electrolyte with $\sigma_+ = 6.2$ Å and $\sigma_- = 3.82$ Å. The osmotic coefficient from Pitzer's treatment is just above the MSA. Circles: MC data from Ref. 1 (system S104); Crosses: experimental data for LaCl_3 aqueous solution [4]; Solid lines: MSA; Dashed lines: Pitzer; Dotted lines: DH.

Next, further results are given below for a comparison of MC data (taken from Abbas et al. [1]) and theories considered in the paper.

In each figure the cation and anion have equal diameters. Those results complement those of the paper in which the cation and anion sizes were chosen on the basis of their maximum asymmetry.

The first two figures are for 1-1 salts, and the other two are for 2-1 salts. In each figure, experimental data are included.

In Figure S4, the diameter of the ions is the smaller of the 1-1 salts treated in Ref. 1. In Figure S5, it is the larger diameter. The same holds for the case of 2-1 salts in Figures S6 and S7, respectively.

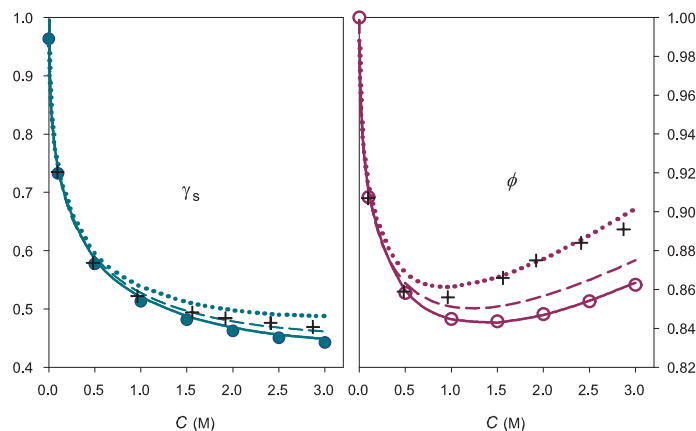


Figure S4: Mean salt activity ($\ln(\gamma_s)$, left panel) and osmotic (right) coefficients for a 1-1 electrolyte with $\sigma_+ = \sigma_- = 2.24 \text{ \AA}$. Circles: MC data from Ref. 1 (system S73); Crosses: experimental data for LiOH aqueous solution [2]; Solid lines: MSA; Dashed lines: Pitzer; Dotted lines: DH.

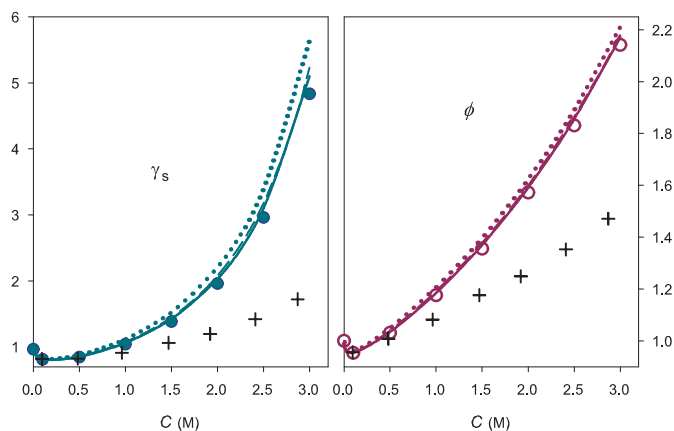


Figure S5: Mean salt activity (left) and osmotic (right) coefficients for a 1-1 electrolyte with $\sigma_+ = \sigma_- = 4.65 \text{ \AA}$. Circles: MC data from Ref. 1 (system S15); Crosses: experimental data for LiI aqueous solution [2]; Solid lines: MSA; Dashed lines: Pitzer; Dotted lines: DH. The Pitzer result for Φ cannot be distinguished from the MSA.

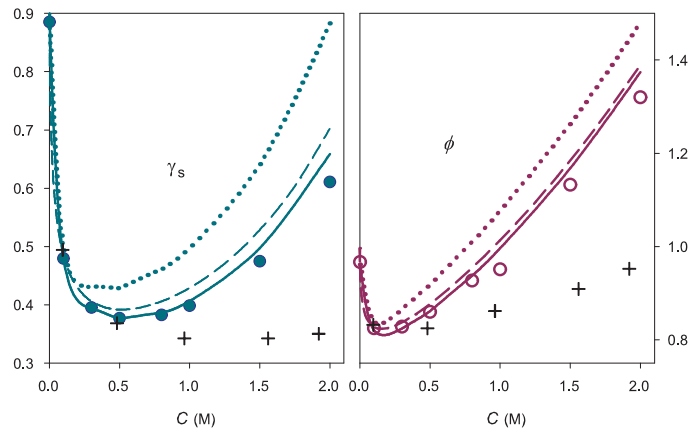


Figure S6: Mean salt activity (left) and osmotic (right) coefficients for a 2-1 electrolyte with $\sigma_+ = \sigma_- = 4 \text{ \AA}$. Symbols: MC data from Ref. 1 (system S55); Crosses: experimental data for $\text{Ca}(\text{NO}_3)_2$ aqueous solution [5]; Solid lines: MSA; Dashed lines: Pitzer; Dotted lines: DH.

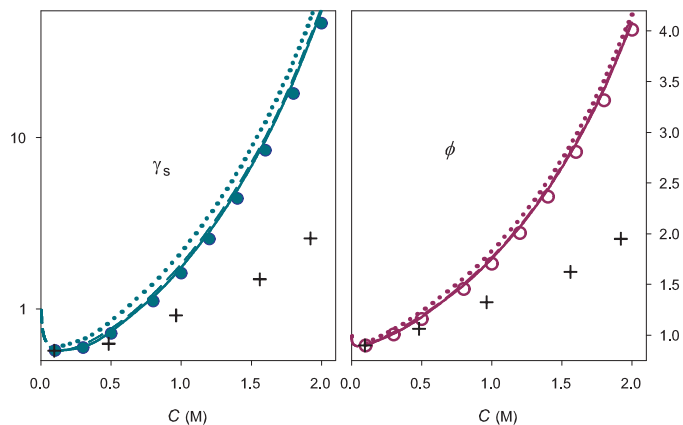


Figure S7: Mean salt activity (left) and osmotic (right) coefficients for a 2-1 electrolyte with $\sigma_+ = \sigma_- = 5.5 \text{ \AA}$. Symbols: MC data from Ref. 1 (system S43); Crosses: experimental data for $\text{Mg}(\text{ClO}_4)_2$ aqueous solution [6]; Solid lines: MSA; Dashed lines: Pitzer; Dotted lines: DH.

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