



HAL
open science

Theory of charge asymmetric electrolytes. Onsager's approach revisited

O. Bernard

► **To cite this version:**

O. Bernard. Theory of charge asymmetric electrolytes. Onsager's approach revisited. Journal of Molecular Liquids, 2022, 366, pp.120163. 10.1016/j.molliq.2022.120163 . hal-03775315

HAL Id: hal-03775315

<https://hal.sorbonne-universite.fr/hal-03775315v1>

Submitted on 12 Sep 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Theory of charge asymmetric electrolytes. Onsager's approach revisited.

O. Bernard^a

^a CNRS, Laboratoire PHENIX, Sorbonne Université (Campus P. et M. Curie), 4, Place Jussieu, Case 51, F-75005 Paris, France.

E-mail address: olivier.bernard@sorbonne-universite.fr

Keywords: Asymmetric electrolytes, Thermodynamic properties, Non-linear theory, Electrostatic association.

Abstract

Onsager made corrections to the Poisson-Boltzmann equation, to more correctly describe interactions in asymmetric electrolytes (those which have different charges, in absolute value, for the cation and the anion). The equations established by Onsager allow the calculation of symmetric total correlation functions, such that $h_{ij}(r) = h_{ji}(r)$. In this article it has been shown that these correlation functions, describing in particular asymmetric electrolytes, can also be deduced from the Ornstein Zernicke integral equations by considering a nonlinear closure relation of the HNC type. The excess free energy deduced from these correlation functions has been found similar to that obtained in Mayer's theory. Relations with the electrostatic association models on the one hand, and with the dressed ions theory on the other hand, are recovered.

1 Introduction

The description of thermodynamic properties of electrolytes has given rise to many developments since the establishment of limiting laws by Debye and Hückel (DH) [1–3]. This theory continues to inspire studies and extensions today [4–8]. Debye and Hückel have used the Poisson-Boltzmann (PB) equations as a starting point to describe the interactions between ions in the solution. By linearizing these equations, analytical expressions of the electrostatic potential ψ_i around an ion i were obtained. Then, the activity coefficients were determined from the expression obtained for the potential. In particular for point ions, a limiting law in square root of the concentration, was established for the variation of the mean activity coefficient. This law is only applicable for small electrolytes, weakly charged, very diluted in a solvent of high dielectric constant. Then, taking into account a minimum distance of approach, as a boundary condition when establishing the expression of the electrostatic potential, DH obtained a modeling of the activity coefficients at higher concentrations. A few years later, it was noted that one of the weaknesses of the DH theory came from the short-range linearization of the equations describing the interactions between ions [9]. In particular Bjerrum proposed an alternative description of the

interactions between unlike ions at low concentrations. Bjerrum assumed that due to the strong attractive interactions between these ions at short distances, ion pairs can form. Then, the free ions are fewer and the DH expressions for the potential and the activity coefficients are modified. This phenomenon is particularly important when the ions are more charged and when the dielectric constant of the solvent is low. As an alternative to the Bjerrum model, corrections to the DH model have been made using perturbation calculations of the neglected terms during the linearization of the PB equations [10–12]. This type of computation turned out to be complicated and was little used thereafter to describe the thermodynamic properties of real solutions. These approaches have been rarely applied due to the poor existing numerical tools when they were established. They seem difficult to use at high concentrations, contrary to Bjerrum’s association theory. Nevertheless, taking into account of the electrostatic screening, they provide a more rigorous theoretical description at low concentrations. Furthermore, Onsager made improvements on these perturbation calculations by adding corrections to the PB equation [13].

Following the cluster expansion theory of McMillan and Mayer [14], statistical mechanics has been applied to the description of solutes in a solvent seen as a continuum. The interaction potentials between charged solutes are assumed to be representative of averages over the configurations of the surrounding solvent. As an application of the McMillan and Mayer cluster expansion, the Mayer theory allowed to determine corrections to the DH results for thermodynamic quantities such as the excess free energy or the osmotic pressure [15]. Additionally, advances in the description of interactions have been made using Ornstein Zernicke (OZ) integral equations to describe the distribution of ions in solution [16]. In particular, the use of the mean spherical approximation (MSA) as a closure relation to these integral equations has led to an analytical modeling of the thermodynamic quantities applicable to higher concentrations than that given by the DH theory [17–22]. The development of the numerical resolution of integral equations associated with more elaborate closure relations [16, 23–25] and later of simulations, by the Monte Carlo method or by molecular dynamics, provides an almost exact description of the thermodynamics of charged solutes for given interaction potentials [26–28]. However, because of the complexity of numerical computations, it is always necessary to have

analytical models to describe the properties of ions in solution. In thermodynamic modeling, even when the solvent is taken into account explicitly, theories representing ions as charged solutes in a continuum continue to be useful to account for their interactions. The MSA theory provides improvements over that of Debye and Hückel to describe long-range interactions. In addition, progress has been made thanks to the association model for symmetric electrolytes. On the other hand, the description of asymmetric electrolytes is less complete (asymmetric binary electrolytes are those in which the absolute value of the charge of cations and anions are different). Then, in the work presented in this article, corrections made by Onsager in the description of asymmetric electrolytes have been considered again. Onsager derived his results from the Poisson Boltzmann equations. It is well known that these equations do not describe in a symmetrical way the interactions between the ions contrary to the OZ integral equations. So it seemed interesting to recover Onsager's corrections for asymmetric electrolytes using both integral equations and statistical mechanics tools.

This article is dedicated to the memory of D. Henderson, who made very significant contributions in the physics of liquids and more particularly to the theory of charged double layers of electrolytes.

In the next section, Onsager's approach is recalled. Subsequently, the integral equations are presented. Integral equations representing the excess, with respect to reference distribution functions, are established. In the next section, a perturbative method for solving these excess integral equations is explained. Thermodynamic properties deduced from these corrective terms are deduced in the following section. Finally, the conclusions and prospects are exposed.

2 Onsager's corrections to the PB equations

Onsager's contribution to the description of asymmetric electrolytes is a correction to the theory of Debye and Hückel. It is therefore necessary to first recall the basis of this theory and the approximations used by these authors to obtain analytical results. As mentioned before, the DH theory is inspired by the earlier work of Gouy and Chapman [29,30]. The

so-called Poisson-Boltzmann equations were introduced in these latter works. In these models the solvent is described as a continuum uniquely characterized by its dielectric constant ϵ_r . The Poisson equation is used to relate an average electrostatic potential ψ_i around an ion i to the distribution of charged species in its environment.

$$\Delta\psi_i = -\frac{4\pi}{\epsilon} \sum_k n_k e_k g_{ik}(r) \quad (1)$$

Where $e_k = z_k e$ is the charge of an ion k , with z_k the valence of this ion, e the charge of the proton and $\epsilon = 4\pi\epsilon_o\epsilon_r$ where ϵ_o designates the vacuum dielectric constant and ϵ_r the dielectric constant of the solvent. Moreover, n_k denotes the concentration of the ions k and $g_{ik}(r)$ the radial distribution function of the ions k at the distance r from the ion i . The function $g_{ik}(r)$ is often defined using the mean force interaction potential $w_{ik}(r)$ between i and k considering a Boltzmann's distribution

$$g_{ik}(r) = \exp[-\beta w_{ik}(r)] \quad (2)$$

Where $\beta = 1/(k_B T)$ with k_B the Boltzmann's constant and T the temperature. In addition, the hypothesis was made that the average potential $w_{ik}(r)$ can be linked to the electric potential ψ_i by the relation

$$w_{ik}(r) = e_k \psi_i(r) \quad (3)$$

Using these relations to define $g_{ik}(r)$ in the Poisson equation, the Poisson-Boltzmann equation was obtained

$$\Delta\psi_i = -\frac{4\pi}{\epsilon} \sum_k n_k e_k e^{-e_k \beta \psi_i(r)} \quad (4)$$

In order to get an analytical expression of this potential, the exponential intervening to the right of the equality in the preceding equation has been linearized by Debye and Hückel. This simplification implies that the distribution function $g_{ik}(r)$, as defined with eqs. (2) and (3), can be approximated by

$$g_{ik}(r) \simeq e^{-e_k \beta \psi_i(r)} \simeq 1 - e_k \beta \psi_i(r) \quad (5)$$

It leads to the linear differential equation for ψ_i used by DH,

$$\Delta\psi_i - \kappa^2 \psi_i = 0$$

where the square of the Debye's screening parameter κ is given by

$$\kappa^2 = \frac{4\pi\beta}{\epsilon} \sum_k n_k e_k^2 \quad (6)$$

The activity coefficients γ_i of the ions i were later calculated from the expression obtained for the potential ψ_i .

Following the work of Debye and Hückel, some authors have been interested in the effect of the next terms in the expansion of the exponential defining the functions $g_{ij}(r)$ within the Poisson-Boltzmann equation. Thus for a symmetric binary electrolyte, by continuing the series expansion of the exponential beyond the linear term, the following differential equation was obtained [10]

$$\Delta\psi_i - \kappa^2\psi_i = \frac{\beta^2}{6}\kappa^2 \eta_2 (\psi_i)^3 + \mathcal{O}(\psi_i)^5 \quad (7)$$

where

$$\eta_2 = \frac{\sum_k n_k e_k^4}{\sum_k n_k e_k^2} \quad (8)$$

When the terms to the right of equality in equation (7) are neglected, the DH equation is recovered with its analytical expression of the potential ψ_i^{DH} . Then for a symmetric electrolyte, in the differential equation beyond the linear term, the first nonzero term in the exponential expansion is proportional to $(\psi_i)^3$.

On the other hand, for an asymmetric binary electrolyte, the first corrective term deduced from the series expansion of the exponential beyond the linear term is a correction proportional to $(\psi_i)^2$ [11, 12]

$$\Delta\psi_i - \kappa^2\psi_i = -\frac{\beta}{2}\kappa^2 \eta_1 (\psi_i)^2 + \mathcal{O}(\psi_i)^3 \quad (9)$$

with

$$\eta_1 = \frac{\sum_k n_k e_k^3}{\sum_k n_k e_k^2} \quad (10)$$

Similarly, disregarding the terms on the right-hand side of the equality, solving the equation (9) leads to the analytical expression ψ_i^{DH} of the potential. Next in order to make

a correction to the potential deduced from the linearized solution, the term proportional to $(\psi_i)^2$ on the right of the equality in the equation (9) has been evaluated in perturbation [11, 12]. A first correction to the DH potential can be deduced from the differential equation in which $(\psi_i)^2$ in the second member has been approximated by $(\psi_i^{\text{DH}})^2$. From this corrected potential an additional contribution to the activity coefficients has been deduced.

It is at this stage that Onsager, by considering the symmetry of the functions $g_{ij}(r)$, made a modification in the calculation of corrective terms to the expressions of DH. The solution of the DH equation leads to a potential ψ_i^{DH} which is proportional to e_i . Using eq. (5), it can be seen that the function $g_{ij}(r)$ deduced from this potential obtained with the linearized differential equation is indeed symmetric in the exchange between i and j . Now, when the term $(\psi_i)^2$ to the right of the equality is replaced by $(\psi_i^{\text{DH}})^2$, the solution of the differential equation with right-hand side leads to a correction to the potential $\delta\psi_i$ which is proportional to e_i^2 . Using again Eq. (5), a corrective term for $g_{ij}(r)$ is obtained which is proportional to $e_j e_i^2$. Then, Onsager noticed that the calculation of $g_{ij}(r)$ using the Poisson-Boltzmann equation, leads to an asymmetrical expression in the exchange between i and j [13]. In order for $g_{ij}(r)$ to be equal to $g_{ji}(r)$, Onsager required the radial distribution function to have the following expansion:

$$g_{ij}(r) = g_{00}(r) + e_j e_i g_{11}(r) + (e_j^2 e_i + e_j e_i^2) g_{12}(r) + \dots \quad (11)$$

The term $g_{00}(r)$ is the only one remaining when the charges vanish. In the Debye, Hückel and Onsager theories, for distances greater than the least approach distance between the ions (all assumed to be the same size), at low concentrations, this term is considered to be equal to 1. The term $e_j e_i g_{11}(r)$ is closely related to the DH term when $e_i \psi_j(r) = e_j \psi_i(r)$ (with ψ_i proportional to e_i). The next term is the first corrective term for an unsymmetrical electrolyte. In order to satisfy this symmetry in the charge exchange, Onsager introduced a correction with respect to the development deduced from the Poisson-Boltzmann equations. It has been considered that the potential deduced from the calculation in perturbation can be developed in increasing powers of the charge according to

$$\psi_i(r) = e_i \phi_1(r) + e_i^2 \phi_2(r) + \dots \quad (12)$$

Then, coupled differential equations for the reduced potentials ϕ_1 and ϕ_2 were deduced by Onsager as,

$$\Delta\phi_1 - \kappa^2\phi_1 = \kappa^2 \eta_1\phi_2 \quad (13a)$$

$$\Delta\phi_2 - \kappa^2\phi_2 = -\frac{\beta}{2}\kappa^2 \eta_1 (\phi_1)^2 \quad (13b)$$

These equations similar to the previous equation (9) were solved in perturbation. Then Onsager was able to deduce the functions $g_{11}(r)$ and $g_{12}(r)$ appearing in the expression (11) for $g_{ij}(r)$ using the expressions obtained for ϕ_1 and ϕ_2 . We are not going to recall all the formulas introduced by Onsager. The interested reader can refer to the original article. As in previous calculations, in order to solve the system of equations, it is first assumed that ϕ_2 is negligible in Eq. (13a). Then the equation for ϕ_1 returns the solution of DH for the potential. Then Eq. (13b) for ϕ_2 is solved by assuming that ϕ_1 is given by the solution obtained previously. So far this calculation is similar to the one that was done before. Onsager brought two corrections compared to the calculation in perturbation performed previously. First, the relations introduced by Onsager make it possible to obtain an approximation for $g_{12}(r)$ and thus to have a symmetric expression of $g_{ij}(r)$. Moreover, Onsager then took into account the approximation obtained for ϕ_2 in Eq. (13a) for ϕ_1 and deduced a correction to this last function. Then from ϕ_1 a correction to $g_{11}(r)$ could be deduced. Finally, using a Guntelberg charging process, Onsager deduced a correction to the chemical potential of the ions of unsymmetrical electrolytes.

Ultimately, the theoretical approach developed by Onsager to overcome the shortcomings of the PB equation appears both ingenious and quite tedious. Consideration of various types of electrolytes requires the introduction of additional ϕ functions. Indeed, if one also wants to evaluate the first corrective term appearing in Eq. (7) for symmetrical electrolytes we have to introduce a function ϕ_3 . Similarly, shorter range contributions also require the introduction of new functions. Moreover, this approach is closely related to the description of the ionic distributions only in terms of electrostatic potential. The Poisson-Boltzmann equations are well suited to evaluate correlation functions when the species under study are assumed to be subject only to Coulomb interactions. Currently, in order to also take into account other types of interactions, (Lennard-Jones potential or

hard spheres repulsion for example), the statistical physics of liquids often prefers to use integral equations to determine the total correlation functions $h_{ij}(r) = g_{ij}(r) - 1$. These integral equations are known to lead to symmetric $h_{ij}(r)$ correlation functions. This symmetry property should make it easier to find corrective terms of the type introduced by Onsager for asymmetric electrolytes. Then, in the following section, it will be presented how the type of distribution function given by Eq. (11) can be established within the framework of integral equations.

3 Integral equations

In order to take into account the interactions between the ions, the total correlation functions $h_{ij}(r)$ are evaluated using the integral equations of Ornstein and Zernike (OZ) instead of the Poisson-Boltzmann equations.

$$h_{ij}(r) = c_{ij}(r) + \sum_k n_k \int c_{ik}(|\mathbf{r} - \mathbf{r}'|) h_{kj}(r') d\mathbf{r}' \quad (14)$$

As a starting point, to find the development of the distribution functions in increasing charges, as given in Eq. (11), we must be able to recover the DH expression of the correlation functions from the OZ equations. This expression can be seen as the zero-order approximation in the perturbation expansion described by Onsager, since the higher-order terms were evaluated, starting from the DH expression, after the expansion of the exponential in the PB Eq. (4). In the context of integral equations, the DH expression of the correlation functions will also constitute a first step to subsequently establish distribution functions having the type of development in increasing charges as given by Eq. (11). We will limit ourselves to the experimental conditions considered in the Onsager's study, namely a weakly charged and very dilute electrolyte. Under these conditions the Debye length is greater than both the Bjerrum length L_B ($L_B = e^2\beta/\epsilon$) and the size of the ions. All the ions are of the same diameter σ . The solution is sufficiently diluted so that the hard sphere contribution to the correlation functions can be considered negligible compared to the electrostatic corrections. This condition is different from that used

by Stell and Lebowitz [31]. In their expansion procedure the uncharged short distance contribution was taken as a known reference.

It is well known that the OZ convolution equations are more easily solvable using Fourier transforms of the functions $h_{ij}(r)$ and $c_{ij}(r)$. We define the Fourier transform $\hat{f}(q)$ of a purely radial function $f(r)$ using the following integral

$$\hat{f}(q) = \frac{4\pi}{q} \int_0^\infty r f(r) \sin(qr) dr \quad (15)$$

where $f(r)$ represents one of the functions $h_{ij}(r)$ or $c_{ij}(r)$. Applying the Fourier transform to the OZ equations allows to replace the convolution products between the correlation functions into simple products of Fourier transforms of these correlation functions.

$$\hat{h}_{ij}(q) = \hat{c}_{ij}(q) + \sum_k n_k \hat{c}_{ik}(q) \hat{h}_{kj}(q) \quad (16)$$

Closure relations are needed to solve the OZ integral equations. The mean spherical approximation (MSA) has been used as the closure relation of the OZ equations to describe electrolyte solutions [17–22]. When ions are modeled as charged hard spheres, this approximation provides analytical expressions for the activity and osmotic coefficients which satisfy the limiting laws of Debye and Hückel at low concentrations and better takes into account the size of the ions at high concentrations [21]. However, to simplify in a first attempt, we will consider point ions, which facilitates the resolution of the equations. Under these conditions the MSA approximation, used to define a first approximation of the direct correlation functions $c_{ij}(r)$ between the ions i and j is given simply by

$$c_{ij}^{\text{MSA}}(r) = -\beta V_{ij}(r) \quad (17)$$

where $V_{ij}(r) = e_i e_j / (\epsilon r)$, is the Coulomb potential between these ions. It is recalled that when the ions are not point-like, the relation (17) is only used for the distances $r > \sigma$. The Fourier transform $\hat{c}_{ij}(q)$ of the Eq. (17) is given by

$$\hat{c}_{ij}(q) = -4\pi \frac{\beta e_i e_j}{\epsilon q^2} \quad (18)$$

The use of this approximation for $\hat{c}_{ij}(q)$ in the Fourier transform of the OZ equations allows to determine an approximate expression $\hat{h}_{ij}^0(q)$ of the total correlation functions,

given by

$$\hat{h}_{ij}^0(q) = -4\pi \frac{\beta e_i e_j}{\epsilon (q^2 + \kappa^2)} \quad (19)$$

Using the inverse Fourier transformation it is possible to determine the corresponding function $h_{ij}^0(r)$. Thus the DH expressions for the total correlation functions of point-like ions are recovered.

$$h_{ij}^0(r) = -\frac{\beta e_i e_j}{\epsilon r} e^{-\kappa r} \quad (20)$$

3.1 Non-linear closure relation

The MSA closure relation linearizes the integral equations in order to obtain analytical results. However, by using integral equations, in order to be able to account for the type of thermodynamic correction presented by Onsager, it is necessary to take into consideration the influence of nonlinear effects of the ionic interactions, in the form of a nonlinear closure relation for the Ornstein-Zernicke equations. We will decompose the functions $c_{ij}(r)$ using the relation

$$c_{ij}(r) = c_{ij}^{\text{MSA}}(r) + c_{ij}^{\text{E}}(r) \quad (21)$$

It is recalled that when the ions are points, $c_{ij}^{\text{MSA}}(r)$ is given by the relation (17) for all distances. Thus, this relation introduces the excess direct correlation function $c_{ij}^{\text{E}}(r)$ with respect to the closure relation previously used. The hypernetted chains relation [23–25] is known to describe accurately the structure and thermodynamics of electrolytes in solution. The HNC closure is given by

$$\ln g_{ij}(r) = -\beta V_{ij}(r) + h_{ij} - c_{ij}(r) \quad (22)$$

If we also use the relation between the mean force potential $w_{ij}(r)$ and $g_{ij}(r)$ given by Eq. (2), we obtain the following relation between $c_{ij}^{\text{E}}(r)$ and $w_{ij}(r)$

$$c_{ij}^{\text{E}}(r) = \exp[-\beta w_{ij}(r)] - 1 + \beta w_{ij}(r) \quad (23a)$$

$$= \sum_{n=2}^{\infty} \frac{(-\beta w_{ij}(r))^n}{n!} \quad (23b)$$

For point ions, in order to have an explicit approximation, the potential of mean force $w_{ij}(r)$ can be replaced by its DH expression deduced from Eq. (20), namely $\beta w_{ij}(r) = -h_{ij}^0(r)$. This approximation has been called extended mean spherical approximation (EMSA) in other studies [32, 35, 36]. In particular, when we limit the sum appearing in Eq. (23) to its first term ($n = 2$), we obtain

$$c_{ij}^E(r) \simeq \frac{\beta^2}{2} \left(w_{ij}(r) \right)^2 \quad (24)$$

This approximation has been used previously in studies of asymmetric electrolytes [37, 38]. If it is recalled that in the DH approximation, we have $w_{ij}(r) = -e_i \psi_j$, then by using equation (24) $c_{ij}^E(r)$ is proportional to $e_i^2 \psi_j^2$. So, using this approximation for $c_{ij}^E(r)$ we take into account corrections proportional to ψ_j^2 as in Eqs. (9) and (13b).

3.2 Excess integral equations

In order to make easier the determination of corrections made to the function $\hat{h}_{ij}(q)$, due to the consideration of the excess function $\hat{c}_{ij}^E(q)$, it is possible to perform a transformation of the OZ equations. The goal is to rewrite the function $\hat{h}_{ij}(q)$ as the sum of a reference function $\hat{h}_{ij}^{\text{ref}}(q)$ previously determined with $\hat{c}_{ij}^E(q) = 0$ and an excess function $\delta \hat{h}_{ij}(q)$ induced by the function $\hat{c}_{ij}^E(q)$. Then for point ions, by replacing in the OZ equations, $c_{ij}(r)$ by the relation (21) we obtain

$$\hat{h}_{ij}(q) = -\frac{4\pi\beta}{\epsilon q^2} e_i \left(e_j + \sum_k n_k e_k \hat{h}_{kj}(q) \right) + \hat{c}_{ij}^E(q) + \sum_k n_k \hat{c}_{ik}^E(q) \hat{h}_{kj}(q) \quad (25)$$

After multiplication by $n_i e_i$, a summation over i of the equations allows to rewrite the first sum over the functions $\hat{h}_{kj}(q)$, to the right of the equality, according to the excess correlation functions and the DH functions $\hat{h}_{kj}^0(q)$. This rearrangement of the Eq. (25) gives

$$\hat{h}_{ij}(q) = \hat{h}_{ij}^0(q) + \hat{c}_{ij}^E(q) + \sum_k n_k \left[\hat{c}_{ik}^E(q) \hat{h}_{kj}(q) + \hat{h}_{ik}^0(q) \left(\hat{c}_{kj}^E(q) + \sum_l n_l \hat{c}_{kl}^E(q) \hat{h}_{lj}(q) \right) \right] \quad (26)$$

This equation makes it easier to separate the functions $\hat{h}_{ij}(q)$ into a reference term $\hat{h}_{ij}^{\text{ref}}(q)$ (here, it is $\hat{h}_{ij}^0(q)$), and corrective terms depending on the excess functions $\hat{c}_{ij}^E(q)$. It

should be noted that this separation can be established with other reference functions. For example if the ions are considered as hard charged spheres, Eq. (21) for $c_{ij}(r)$ can still be used and by following the same rearrangement as before, we obtain an equation similar to Eq. (26) for $\hat{h}_{ij}(q)$ but with the functions $\hat{h}_{ij}^0(q)$ replaced by $\hat{h}_{ij}^{\text{MSA}}(q)$ (see Appendix A).

At this stage, our goal is to find, from the integral equations, distribution functions similar to those obtained by Onsager. To do this, we will start from the excess integral equations (26). We will deduce from these equations, differential equations applicable to low concentrations.

4 Perturbative expansion

It has been shown that the excess integral equations can be obtained starting either from the functions $\hat{h}_{ij}^0(q)$, or from the functions $\hat{h}_{ij}^{\text{MSA}}(q)$. Moreover, it has been shown that the distribution functions obtained with the MSA tend towards those given by the DH expressions at low concentrations [21]. Compared to those of Debye and Hückel, the distribution functions obtained with the MSA are applicable to high concentrations. However at high concentrations, the distribution functions obtained from the MSA can no longer be represented with a single exponential function like those of Debye and Hückel. In particular, oscillations are observed above some concentration. In his perturbation expansion, Onsager took as initial distribution functions those given by Debye and Hückel. Since we limit ourselves to low concentrations, to simplify and in order to consider only one screening length, we will therefore take in the rest of this study an initial distribution function of the type of those given by Debye and Hückel.

Now, in order to initiate the perturbative expansion, we split the function $\hat{h}_{ij}(q)$ into two contributions

$$\hat{h}_{ij}(q) = \hat{h}_{ij}^0(q) + \delta\hat{h}_{ij}(q) \quad (27)$$

Then, as a starting point, it will be assumed that the functions $\hat{h}_{ij}^0(q)$ can be seen as a good approximation of the correlation functions $\hat{h}_{ij}(q)$. So we can replace $\hat{h}_{ij}(q)$ with

$\hat{h}_{ij}^0(q)$ in the terms to the right of equality in equation (26). This leads to a first correction which can be separated into three term:

$$\delta\hat{h}_{ij}(q) = \delta\hat{h}_{ij}^{(1)}(q) + \delta\hat{h}_{ij}^{(2)}(q) + \delta\hat{h}_{ij}^{(3)}(q) \quad (28)$$

with

$$\delta\hat{h}_{ij}^{(1)}(q) = \hat{c}_{ij}^E(q) \quad (29a)$$

$$\delta\hat{h}_{ij}^{(2)}(q) = \sum_k n_k \left[\hat{c}_{ik}^E(q) \hat{h}_{kj}^0(q) + \hat{h}_{ik}^0(q) \hat{c}_{kj}^E(q) \right] \quad (29b)$$

$$\delta\hat{h}_{ij}^{(3)}(q) = \sum_k n_k \hat{h}_{ik}^0(q) \sum_l n_l \hat{c}_{kl}^E(q) \hat{h}_{lj}^0(q) \quad (29c)$$

It is observed that this expression is symmetric for the inversion of the indices i and j . We note that each of the three terms is proportional to a function $\hat{c}_{ij}^E(q)$. A remark can be made on this approximation. For simplicity, it seems tempting to limit ourselves to the first corrective term and to consider that $\delta\hat{h}_{ij}(q) \simeq \hat{c}_{ij}^E(q)$. This immediately leads to $\delta h_{ij}(r) \simeq c_{ij}^E(r)$. When the Eq. (23) is used to define the direct correlation functions $c_{ij}^E(r)$, this leads to a so-called exponential approximation of the Debye and Hückel potential which has been used before. However, whatever the choice made to define $c_{ij}^E(r)$, the fact of considering that $\delta h_{ij}(r) \simeq c_{ij}^E(r)$, implies that electroneutrality is no longer preserved. Indeed, the electroneutrality condition can be computed from the functions $\hat{h}_{ij}(q)$ by taking the limit where q tends to zero.

$$\sum_j n_j e_j \hat{h}_{ij}(0) = -e_i \quad (30)$$

If it is assumed that $\delta\hat{h}_{ij}(q) = \hat{c}_{ij}^E(q)$, then it is found that the relationship (30) is not verified. On the other hand, if $\delta\hat{h}_{ij}(q)$ is given by Eq. (28), then the electroneutrality relation (30) holds regardless of the definition chosen for $c_{ij}^E(r)$.

In this section, in order to find expressions like those of Onsager, the perturbation computation was limited to the first order power of $\hat{c}_{ij}^E(q)$. In the last section we will return to the study of the influence of higher order terms in a power expansion of $\hat{c}_{ij}^E(q)$.

4.1 Approximate correlation functions

First, it is obvious that $\delta h_{ij}^{(1)}(r)$, the inverse Fourier transform of $\delta \hat{h}_{ij}^{(1)}(q)$, is the function $c_{ij}^E(r)$. If this function is approximated by the expression (24), we find the first corrective term coming from the expansion to order two of the PB equation (4), as it is used in the equation (9).

Next, in order to be able to obtain an expression of $\delta h_{ij}^{(2)}(r)$, a differential equation has been deduced from the equation (29b). As a starting point, equation (29b) has been multiplied on either side of the equality by the denominator of the functions $\hat{h}_{ij}^0(q)$, namely $(q^2 + \kappa^2)$. Then, the following relation has been introduced:

$$\delta h_{ij}^{(2)}(r) = e_i \Phi_j(r) + e_j \Phi_i(r) \quad (31)$$

with the following differential equation:

$$(\Delta - \kappa^2) \Phi_j(r) = \frac{4\pi}{\epsilon} \beta \sum_k n_k e_k c_{jk}^E(r) \quad (32)$$

Here, it has been used that the Fourier transform of $\Delta \Phi_j(r)$ is given by $-q^2 \hat{\Phi}_j(q)$. Solving Eq. (32) allows us to determine $\delta h_{ij}^{(2)}(r)$ when an explicit expression of $c_{ij}^E(r)$ is given. When $c_{ij}^E(r)$ is evaluated using the Eq. (24), we find a contribution to $\delta h_{ij}(r)$, proportional to $(e_i^2 e_j + e_i e_j^2)$ like the one that can be deduced from the Eq. (11).

Next, to simplify the evaluation of $\delta h_{ij}^{(3)}(r)$ it is noted that the Eq. (29c) can be rewritten, given the expressions (31) and (32) deduced from $\delta \hat{h}_{ij}^{(2)}(q)$, following

$$\delta \hat{h}_{ij}^{(3)}(q) = e_j \sum_k n_k \hat{h}_{ik}^0(q) \hat{\Phi}_k(q) \quad (33)$$

As before both sides of this equation can be multiplied by $(q^2 + \kappa^2)$, and the following differential equation is found

$$(\Delta - \kappa^2) \delta h_{ij}^{(3)}(r) = \frac{4\pi}{\epsilon} \beta e_i e_j \sum_k n_k e_k \Phi_k(r) \quad (34)$$

It is noted that this corrective term is proportional to $e_i e_j$. When the Eq. (24) is used again to define $c_{ij}^E(r)$, this term corresponds to the second correction found by Onsager.

In order to determine the functions $\delta h_{ij}(r)$, it is necessary to impose boundary conditions to complete these differential equations. It is of course imposed that the functions $\delta h_{ij}(r)$ are finite when the distance r tends to infinity. Furthermore, for its calculation, Onsager used as a starting function the DH expression of the potential $\psi_i^{\text{DH}}(r)$, which takes into account a distance of least approach. The corresponding DH correlation function $h_{ij}^{\text{DH}}(r)$ is deduced from Eq. (5), (with ψ_i replaced by ψ_i^{DH})

$$h_{ij}^{\text{DH}}(r) = -\frac{\beta e_i e_j}{\epsilon(1 + \kappa\sigma)r} e^{-\kappa(r-\sigma)} \quad (35)$$

Therefore, this correlation function has been used as a starting point to evaluate the correction $\delta h_{ij}(r)$. From this reference function, the function $w_{ij}(r)$ was determined using the relation: $-\beta w_{ij}(r) = h_{ij}^{\text{DH}}(r)$. Then $c_{ij}^{\text{E}}(r)$ can be defined as a function of $w_{ij}(r)$ using Eq. (23), or alternatively Eq. (24) if one wishes to be satisfied with the first term of the limited development of the previous equation. In this way, the first contribution $\delta h_{ij}^{(1)}(r)$ can be immediately determined as before from the corresponding definition of $c_{ij}^{\text{E}}(r)$. In order to integrate the differential equations (32) and (34) we have adopted the boundary conditions at $r = \sigma$ introduced by Onsager which allows to determine the two other contributions to $\delta h_{ij}(r)$. More details and useful expressions to evaluate $\delta h_{ij}^{(2)}(r)$ and $\delta h_{ij}^{(3)}(r)$ are given in Appendix B. Once the $\delta h_{ij}(r)$ functions have been determined, it is possible to evaluate their effects on the thermodynamic quantities.

5 Thermodynamics

Several thermodynamic quantities can be evaluated from integrals which depend on the total correlation functions $h_{ij}(r)$. Due to the approximations used to express $h_{ij}(r)$, all possible quantities are not calculated with the same precision. For electrolyte solutions it is well known that the internal energy can be relatively well described from the functions $h_{ij}^{\text{DH}}(r)$. Then, it is interesting to determine the contribution to the internal energy due to the functions $\delta h_{ij}(r)$.

5.1 The internal energy

The variation of the internal energy due to the functions $\delta h_{ij}(r)$ can be computed with the following formula

$$\begin{aligned}\Delta E &= 2\pi \sum_{i,j} n_i n_j \int_{\sigma}^{\infty} r V_{ij}(r) \delta h_{ij}(r) dr \\ &= \frac{2\pi}{\epsilon} \sum_{i,j} n_i e_i n_j e_j \int_{\sigma}^{\infty} r \delta h_{ij}(r) dr\end{aligned}\quad (36)$$

Taking into account the three contributions of $\delta h_{ij}(r)$ is quite tedious but straightforward. Strong term compensations were found between the three contributions. The boundary conditions have been used to simplify the evaluation of the various contributions. More details have been presented in Appendix C.1. It was eventually found

$$\Delta E = \frac{2\pi}{\epsilon} \sum_{i,j} n_i e_i n_j e_j \int_{\sigma}^{\infty} r \mathcal{F}_{ij}(r) dr \quad (37)$$

with

$$\mathcal{F}_{ij}(r) = \frac{1}{1 + \kappa\sigma} e^{-\kappa(r-\sigma)} \left(1 - \frac{1}{2}\kappa r + \frac{\kappa^2\sigma^2}{2(1 + \kappa\sigma)} \right) c_{ij}^E(r) \quad (38)$$

It is recalled that $c_{ij}^E(r)$ can be defined as a function of $w_{ij}(r)$ using Eq. (23), or alternatively Eq. (24).

5.2 The Helmholtz free energy

The Helmholtz free energy can be deduced from the internal energy using a Kirkwood charging process.

$$\begin{aligned}\Delta A &= \frac{2\pi}{\epsilon} \sum_{i,j} n_i e_i n_j e_j \int_0^1 d\lambda \int_{\sigma}^{\infty} r \delta h_{ij}(\lambda, r) dr \\ &= \frac{2\pi}{\epsilon} \sum_{i,j} n_i e_i n_j e_j \int_0^1 d\lambda \int_{\sigma}^{\infty} r \mathcal{F}_{ij}(\lambda, r) dr\end{aligned}\quad (39)$$

Here $\delta h_{ij}(\lambda, r)$ represents the function $\delta h_{ij}(r)$ for which the set of charges e_k have been replaced by $\lambda^{1/2}e_k$. Consequently the parameter κ is also replaced by $\lambda^{1/2}\kappa$. Similarly $\mathcal{F}_{ij}(\lambda, r)$ represents the function $\mathcal{F}_{ij}(r)$ in which all charges e_k are replaced by $\lambda^{1/2}e_k$, with

also κ replaced by $\lambda^{1/2}\kappa$. Since $\mathcal{F}_{ij}(r)$ is given by eq. (38), then $\mathcal{F}_{ij}(\lambda, r)$ is proportional to $c_{ij}^E(\lambda, r)$. In order to perform the thermodynamic integration on λ , it is necessary to provide an explicit expression of these excess direct correlation functions. The expression (23) was used. In this particular case it was found that the thermodynamic integration can be carried out explicitly. This leads to a relatively simple expression for the excess of the Helmholtz free energy ΔA (see Appendix C.2).

$$\beta\Delta A = -2\pi \sum_{i,j} n_i n_j \int_{\sigma}^{\infty} \left[e^{-\beta w_{ij}(r)} - \mathcal{E}_2(-\beta w_{ij}(r)) \right] r^2 dr \quad (40)$$

with $\beta w_{ij}(r) = -h_{ij}^{\text{DH}}(r)$, and

$$\mathcal{E}_N(x) = \sum_{k=0}^N \frac{x^k}{k!} \quad (41)$$

This result presents similarities with the expression of the Helmholtz free energy obtained within the framework of the so-called DHLL+B₂ theory [16, 39–41].

$$-\beta(A^{\text{ex}})_{\text{DHLL+B}_2} = \frac{\kappa^3}{12\pi} + \sum_{i,j} n_i n_j B_{ij}(\kappa) \quad (42)$$

where the second virial coefficient $B_{ij}(\kappa)$ has the form

$$B_{ij}(\kappa) = 2\pi \int_0^{\infty} \left[e^{-\beta(u_{ij}^{\text{HS}}(r) + w_{ij}^0(r))} - \mathcal{E}_2(-\beta w_{ij}^0(r)) \right] r^2 dr \quad (43)$$

in which $u_{ij}^{\text{HS}}(r)$ is the hard sphere potential and $\beta w_{ij}^0(r) = -h_{ij}^0(r)$. This equation results from the application to electrolytes of the thermodynamic density expansion due to Mayer [15]. In Eq. (42), the first term (proportional to κ^3), is the contribution to the free energy obtained in the theory of Debye and Hückel for point ions, namely the Debye and Hückel limiting law (DHLL). By contrast, it should be noted that in this present study, the free energy ΔA given by Eq. (40) is an excess term over the contribution obtained in the Debye and Hückel theory taking into account the excluded volume of the ions. In Eq. (42), the second term (proportional to $B_{ij}(\kappa)$) is very similar to the free energy ΔA given by Eq. (40). The excess term given by Eq. (40) can be compared to the contribution for distances larger than σ deduced from the equation for $B_{ij}(\kappa)$. For these distances the two expressions are almost identical except that $w_{ij}^0(r)$ appearing in Eq. (43)

is replaced by $w_{ij}(r)$ in Eq. (40). The thermodynamic cluster expansions deduced from Mayer's theory have been used to establish series in increasing power of the concentration beyond the limiting law of Debye and Hückel [42, 43]. Thermodynamic developments of the DHLL+B₂ type are especially applicable at low concentrations [40, 44]. It has been shown that in order to better describe the thermodynamics at high concentrations it is necessary to take into account higher order virial coefficients which are more difficult to evaluate, beyond the B₂ terms [39].

Since our initial goal was to find the specific thermodynamic contribution of asymmetric electrolytes, the excess free energy $\beta\Delta A$ is separated into two parts, namely the asymmetric contribution $\beta\Delta A_2$ and the remainder of the excess free energy $\beta\Delta A_{\text{SR}}$, which is assumed to be a contribution from shorter distances. The part $\beta\Delta A_2$ can be deduced when only the first term of the series expansion of the term between square brackets in Eq. (40) is retained.

$$\beta\Delta A_2 = \frac{\pi}{3} \left(\frac{\beta}{\epsilon(1 + \kappa\sigma)} \right)^3 \left(\sum_k n_k e_k^3 \right)^2 e^{3\kappa\sigma} E_1(3\kappa\sigma) \quad (44)$$

with

$$E_1(x) = \int_x^\infty dt \frac{e^{-t}}{t} \quad (45)$$

At high dilution, Eq. (44) tends towards the excess free energy term, proportional to $(\sum_k n_k e_k^3)^2$, as presented in [42, 43].

The shortest range contribution to the excess free energy $\beta\Delta A_{\text{SR}}$ is given by

$$\beta\Delta A_{\text{SR}} = -2\pi \sum_{i,j} n_i n_j \int_\sigma^\infty \left[e^{-\beta w_{ij}(r)} - \mathcal{E}_3(-\beta w_{ij}(r)) \right] r^2 dr \quad (46)$$

Contrary to the previous contribution, this one remains for symmetrical electrolytes. In particular, the integral involved in this expression can also be evaluated in the limit where the concentration tends towards zero. In this limit, the potential $w_{ij}(r)$ is replaced by the Coulomb potential $V_{ij}(r)$. Then, at low concentrations, the term $\beta\Delta A_{\text{SR}}$ becomes proportional to the square of the concentration. Obviously, by differentiation the excess pressure can be deduced from the free energy. At low concentrations, the contribution

to the excess pressure deduced from $\beta\Delta A_{SR}$ is also proportional to the square of the concentration [45]. This attractive electrostatic contribution has been embed in models considering the formation of anion-cation pairs [45, 46].

5.3 Excess osmotic coefficient

From the Helmholtz free energy, the excess pressure and osmotic coefficient can be determined by differentiation. The excess osmotic coefficient $\Delta\varphi$ can be obtained by using the relation

$$\Delta\varphi = \frac{\beta\Delta P}{n} = \sum_k n_k \frac{\partial}{\partial n_k} \left(\frac{\beta\Delta A}{n} \right) \quad (47)$$

where ΔP is the excess pressure deduced from the free energy ΔA and $n = \sum_j n_j$. Starting from $\beta\Delta A$ given by Eq. (40), the osmotic pressure can then be deduced:

$$\beta\Delta P = \beta\Delta A - \frac{\pi\beta}{\epsilon(1+\kappa\sigma)} \sum_{i,j} n_i e_i n_j e_j \int_{\sigma}^{\infty} e^{-\kappa(r-\sigma)} \left(\kappa r - \frac{\kappa^2 \sigma^2}{1+\kappa\sigma} \right) c_{ij}^E(r) r dr \quad (48)$$

The asymmetric contribution $\beta\Delta P_2$ deduced from $\beta\Delta A_2$ is given in Appendix C.3.

Additionally, using Eq. (48), it is found that the shortest range contribution $\beta\Delta P_{SR}$ to the excess pressure, becomes equal to $\beta\Delta A_{SR}$ at very low concentrations. In this limit, the potential $w_{ij}(r)$ is replaced by the Coulomb potential $V_{ij}(r)$. Therefore, $\beta\Delta P_{SR}$ is proportional to the square of the concentration at high dilution. This attractive contribution can be taken into consideration within models involving ionic association. In models considering ion pairs formation, if we denote by n_p the concentration of pairs, then the osmotic excess coefficient contains the additional term: $-n_p/n$. In these models, by imposing that the concentration of ion pairs is equal to $-\beta\Delta P_{SR}$ at high dilution, then this attractive contribution to the pressure is simply taken into consideration [45, 46]. This last approach, both takes into account the development deduced from the thermodynamic cluster expansions, and also describes well the evolution of thermodynamic properties at high concentrations. The modeling of the phase separation in symmetrical electrolytes has been performed with this type of model [47–49].

As an alternative, instead of being determined by free energy differentiation, the contribution to the pressure associated to the functions $\delta h_{ij}(r)$ can be obtained via the virial theorem:

$$\beta\Delta P^v = \frac{2\pi}{3} \sum_{i,j} n_i n_j \sigma^3 \delta h_{ij}(\sigma) + \frac{2\pi}{3\epsilon} \beta \sum_{i,j} n_i e_i n_j e_j \int_{\sigma}^{\infty} \delta h_{ij}(r) r dr \quad (49)$$

The pressure deduced with Eq. (49) represents a correction to the pressure $\beta\Delta P_1^v$, obtained with this same equation, when $h_{ij}^{\text{DH}}(r)$ is considered instead of $\delta h_{ij}(r)$. Significant simplifications have been found when summing the three components of $\delta h_{ij}(\sigma)$ occurring in the first term of Eq. (49). Then, using the definition (36) of the internal energy, ones arrive at

$$\beta\Delta P^v = \frac{2\pi}{3} \sigma^3 \sum_{i,j} n_i n_j c_{ij}^{\text{E}}(\sigma) + \frac{1}{3} \beta \Delta E \quad (50)$$

The contribution $\beta\Delta P_2^v$ obtained from Eq. (50), with $c_{ij}^{\text{E}}(r)$ given by the Eq. (24), is also given in Appendix C.3. Surprisingly, considering that $c_{ij}^{\text{E}}(\sigma)$ is defined by Eq. (24), the first term gives a non-zero contribution for symmetrical electrolytes. As before in $\beta\Delta P_2$ however, the second term $\beta\Delta E_2/3$, deduced from the Eq. (36) is proportional to $(\sum_i n_i e_i^3)^2$. It therefore vanishes for symmetrical electrolytes. When the first term, dependent on the $c_{ij}^{\text{E}}(\sigma)$, in $\beta\Delta P_2^v$ is added to the contribution $\beta\Delta P_1^v$, the expression determined by Pitzer is retrieved [50,51]. Then, the sum of the two terms $\beta(\Delta P_1^v + \Delta P_2^v)$ is equal to the corresponding term determined by Pitzer plus $\beta\Delta E_2/3$.

When the excess pressure is deduced from the free energy, the DH term that remains for symmetric electrolytes, is determined independently of the asymmetric term $\beta\Delta P_2$. On the other hand, when the excess pressure is determined from the virial theorem the various contributions are not separated. Accordingly, the next term in the expansion of $c_{ij}^{\text{E}}(\sigma)$ from Eq. (23) provides also a contribution proportional to $(\sum_i n_i e_i^3)^2$. More details have been presented in Appendix C.3.

6 Conclusion and prospects

Onsager made corrections to the Poisson-Boltzmann equation, to more properly describe interactions in asymmetric electrolytes. His attention focused in particular on the symmetry of correlation functions, such that $h_{ij}(r) = h_{ji}(r)$. The linearized equation of Debye and Hückel is indeed symmetric, since $h_{ij}(r)$ is proportional to the product of the charges $e_i e_j$. It is no longer true, when we consider corrective terms deduced from an expansion in perturbation of the Poisson-Boltzmann equation. To correct this defect, Onsager has established a system of equations allowing to calculate symmetric correlation functions.

In this work it has been shown that these correlation functions, describing in particular asymmetric electrolytes, can also be deduced from the OZ integral equations by considering a nonlinear closure relation of the HNC type. These equations were solved in perturbation, starting from a linearized solution. It should be noted that the approximate calculation, used to explicitly evaluate these correlation functions, satisfies the conditions of electroneutrality. The free energy associated with these correlation functions has been calculated. Surprisingly, the excess free energy, with respect to that of Debye with volume excluded, has a mathematical form similar to that deduced from Mayer's theory. We found the specific contribution of asymmetric electrolytes. Moreover, the contributions from shorter distances, responsible for the electrostatic association, are also recovered.

The excess integral equations were solved in perturbation starting with the DH correlation functions chosen as reference. This limits the application of this study to low concentrations. Other reference functions are possible. In particular, the integral equations describing the excess, when the reference functions are those of the MSA theory, have also been established. They could be used for more concentrated solutions.

Furthermore, changes in the electrostatic screening length compared to that of Debye's theory have been described previously [37, 38, 52–56]. An accurate description of the behavior of screening in binary electrolytes has been obtained by applying the dressed ion theory. The dressed ion theory (DIT) was introduced in particular to extend the field of application of Debye and Hückel's theory [52, 53]. This theory has been also applied

to the description of asymmetric electrolytes [54, 55]. Starting from the excess integral equations (26), an analysis according to the dressed ion theory has been performed. This allowed to assess the effect of higher order terms in a power expansion of $\hat{c}_{ik}^E(q)$ functions. A description of the summation method used is given in Appendix D. This approach led to consider effective charges e_i^* and an effective screening parameter κ_* , instead of bare charges e_i and the Debye screening parameter κ . To make a comparison with the expressions obtained previously, only the result obtained at low concentrations is presented here. In this limit it was found,

$$\hat{h}_{ij}(q) \simeq \hat{c}_{ij}^E(q) - \frac{4\pi}{\epsilon} \beta \frac{e_i^* e_j^*}{q^2 + \kappa_*^2} \quad (51)$$

with

$$e_i^* = e_i + \sum_k n_k e_k \hat{c}_{ik}^E(q) \quad (52)$$

and the effective screening parameter κ_* can be defined from these effective charges

$$\kappa_*^2 = \frac{4\pi}{\epsilon} \beta \sum_i n_i e_i e_i^* \quad (53)$$

In Eq. (51), the second term after $\hat{c}_{ij}^E(q)$, looks like $\hat{h}_{ij}^0(q)$ as given in (19), but with $e_i^* e_j^*$ in place of $e_i e_j$ and κ_*^2 in place of κ^2 . For comparison, the next term after $\hat{c}_{ij}^E(q)$ in Eq. (51), can be expanded to the first order power of $\hat{c}_{ik}^E(q)$. Two terms proportional to $e_i e_j$ are found, which are actually $\hat{h}_{ij}^0(q)$ and $\delta \hat{h}_{ij}^{(3)}(q)$. Then, the function $\delta \hat{h}_{ij}^{(3)}(q)$ represents at low concentrations the effect of the variation of the screening length on the part of the correlation function proportional to $e_i e_j$. When the product $e_i^* e_j^*$ is expanded to first order power of $\hat{c}_{ik}^E(q)$ and $\hat{c}_{jk}^E(q)$, the function $\delta \hat{h}_{ij}^{(2)}(q)$ is also recovered. Then, the functions $\delta \hat{h}_{ij}^{(2)}(q)$ account for the difference between the effective charges e_i^* and the bare charges e_i , to the first order in power of the $\hat{c}_{lk}^E(q)$ functions. Therefore, Onsager's perturbation method, as adapted in this study, provides an alternative approach to evaluate variations in screening length and effective charges.

The approximation used to calculate the correlation functions $\delta \hat{h}_{ij}(q)$ fullfills the electroneutrality relation (deduced when $q \rightarrow 0$). Using the OZ equations, the Stillinger and Lovett relations [57–59] could also be studied, especially when more accurate references

will be used. In addition, the correlation functions $\delta h_{ij}(r)$ obtained in this study could also be used to evaluate the effect of these corrections on transport properties such as electrical conductivity [60].

Appendices :

A Excess integral equations relative to other reference total correlation functions

In this appendix, generalizations are presented for the excess integral equations introduced in section 3.2. Instead of $\hat{h}_{ij}^0(q)$ other total correlation functions have been chosen as reference.

A.1 Debye and Hückel treatment with excluded volume

First the chosen reference correlation function $\hat{h}_{ij}^{\text{ref}}(q)$ is that of Debye and Hückel with excluded volume $\hat{h}_{ij}^{\text{DH}}(q)$, instead of $\hat{h}_{ij}^0(q)$. Indeed, for its perturbation calculation, Onsager used as a starting function the expression of DH, which takes into account a distance of least approach. The Fourier transform of this function is given by:

$$\hat{h}_{ij}^{\text{DH}}(q) = -\frac{4\pi\beta}{\epsilon(1 + \kappa\sigma)(q^2 + \kappa^2)} e_i e_j \left(\cos(q\sigma) + \frac{\kappa}{q} \sin(q\sigma) \right) \quad (54)$$

It can be found that this function is the solution of the following integral equation

$$\hat{h}_{ij}(q) = \hat{c}_{ij}^{\text{DH}}(q) + \sum_k n_k \hat{c}_{ik}^0(q) \hat{h}_{kj}(q) \quad (55)$$

with $\hat{c}_{ik}^0(q)$ given by Eq. (18) and

$$\hat{c}_{ij}^{\text{DH}}(q) = -\frac{4\pi\beta}{\epsilon(1+\kappa\sigma)q^2} e_i e_j \left(\cos(q\sigma) + \frac{\kappa}{q} \sin(q\sigma) \right) \quad (56)$$

or equivalently

$$c_{ij}^{\text{DH}}(r) = \begin{cases} -\frac{\beta}{\epsilon} \frac{\kappa}{1+\kappa\sigma} e_i e_j & \text{if } r < \sigma \\ -\frac{\beta}{\epsilon r} e_i e_j & \text{if } r > \sigma \end{cases} \quad (57)$$

It is observed in Eq. (55) that the effect of the excluded volume is taken into account only for the direct correlation function $\hat{c}_{ij}^{\text{DH}}(q)$. The indirect correlations with the ions k around the ion i remain described with the functions $\hat{c}_{ik}^0(q)$ as for point ions. As it has been noted before, in the DH theory the screening of the surrounding ions does not depend on their size. Next, the introduction of the functions $\hat{c}_{ik}^{\text{E}}(q)$ into Eq. (55) leads to

$$\hat{h}_{ij}(q) = \hat{c}_{ij}^{\text{DH}}(q) + \hat{c}_{ij}^{\text{E}}(q) + \sum_k n_k \left(\hat{c}_{ik}^0(q) + \hat{c}_{ik}^{\text{E}}(q) \right) \hat{h}_{kj}(q) \quad (58)$$

By performing the same transformation used for the point ions it is found

$$\hat{h}_{ij}(q) = \hat{h}_{ij}^{\text{DH}}(q) + \hat{c}_{ij}^{\text{E}}(q) + \sum_k n_k \left[\hat{c}_{ik}^{\text{E}}(q) \hat{h}_{kj}(q) + \hat{h}_{ik}^0(q) \left(\hat{c}_{kj}^{\text{E}}(q) + \sum_l n_l \hat{c}_{kl}^{\text{E}}(q) \hat{h}_{lj}(q) \right) \right] \quad (59)$$

which is similar to Eq. (26) but with the function $\hat{h}_{ij}^0(q)$ after equality, replaced by the function $\hat{h}_{ij}^{\text{DH}}(q)$.

A.2 The mean spherical approximation

Next, to extend this approach to higher concentrations, the chosen reference correlation function $\hat{h}_{ij}^{\text{ref}}(q)$ could be the one given by the MSA theory. For ions of the same size, in the MSA approximation, the direct correlation functions are given by eq. (17) for $r > \sigma$. There is also an additional contribution for $r < \sigma$. For ions of the same size σ , the Fourier transform of $c_{ij}^{\text{MSA}}(r)$ can be separated into two terms as follows

$$\hat{c}_{ij}^{\text{MSA}}(q) = \hat{c}_{00}^{\text{HS}}(q) + \hat{c}_{11}(q) e_i e_j \quad (60)$$

such that $\hat{c}_{00}^{\text{HS}}(q)$ and $\hat{c}_{11}(q)$ are two functions which are independent of i and j . Then, using this relation and the Eq. (21) for $c_{ij}(r)$, starting from the OZ's equations we find

$$\hat{h}_{ij}(q) = \hat{h}_{ij}^{\text{MSA}}(q) + \hat{c}_{ij}^{\text{E}}(q) + \sum_k n_k \left[\hat{c}_{ik}^{\text{E}}(q) \hat{h}_{kj}(q) + \hat{h}_{ik}^{\text{MSA}}(q) \left(\hat{c}_{kj}^{\text{E}}(q) + \sum_l n_l \hat{c}_{kl}^{\text{E}}(q) \hat{h}_{lj}(q) \right) \right] \quad (61)$$

which is similar to Eq. (26) but with all the functions $\hat{h}^0(q)$ replaced by the corresponding functions $\hat{h}^{\text{MSA}}(q)$.

B Integration of the functions $\delta h_{ij}(r)$

In this appendix, the boundary conditions at $r = \sigma$ introduced by Onsager are recovered. This allows to integrate the differential equations (32) and (34) and thus determine the functions $\delta h_{ij}^{(2)}(r)$ and $\delta h_{ij}^{(3)}(r)$.

Starting from the previously determined Eqs. (29b) and (29c), the limit when the variable $q \rightarrow 0$ of each of the contributions to $\delta \hat{h}_{ij}(q)$ leads to the following relations:

$$\int_{\sigma}^{\infty} r^2 \Phi_j(r) dr = -\frac{4\pi\beta}{\epsilon\kappa^2} \sum_k n_k e_k \int_{\sigma}^{\infty} r^2 c_{jk}^{\text{E}}(r) dr \quad (62)$$

$$\int_{\sigma}^{\infty} r^2 \delta h_{ij}^{(3)}(r) dr = -\frac{4\pi\beta}{\epsilon\kappa^2} e_i e_j \sum_k n_k e_k \int_{\sigma}^{\infty} r^2 \Phi_k(r) dr \quad (63)$$

Furthermore, the differential equations (32) and (34) can be written more explicitly as

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial \Phi_j(r)}{\partial r} \right) - \kappa^2 r^2 \Phi_j(r) = \frac{4\pi}{\epsilon} \beta \sum_k n_k e_k r^2 c_{jk}^{\text{E}}(r) \quad (64)$$

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial \delta h_{ij}^{(3)}(r)}{\partial r} \right) - \kappa^2 r^2 \delta h_{ij}^{(3)}(r) = \frac{4\pi}{\epsilon} \beta e_i e_j \sum_k n_k e_k r^2 \Phi_k(r) \quad (65)$$

By using relations (62) and (63), it is found by integration of the differential equation (64) and (65) that

$$\left(\frac{\partial \Phi_j}{\partial r} \right)_{r=\sigma} = 0 \quad (66)$$

and

$$\left(\frac{\partial \delta h_{ij}^{(3)}}{\partial r}\right)_{r=\sigma} = 0 \quad (67)$$

This allows to integrate the differential equations (32) and thus determine the functions $\delta h_{ij}^{(2)}(r)$. The relation (31) is used to express $\delta h_{ij}^{(2)}(r)$ with the $\Phi_j(r)$ functions, for which it is found

$$\Phi_j(r) = -\frac{4\pi}{\epsilon}\beta \sum_k n_k e_k \Psi_{jk}(r) \quad (68)$$

with

$$\Psi_{jk}(r) = \frac{e^{-\kappa r}}{2\kappa r} \int_{\sigma}^r s e^{\kappa s} c_{jk}^E(s) ds + \frac{e^{\kappa r}}{2\kappa r} \int_r^{\infty} s e^{-\kappa s} c_{jk}^E(s) ds + \mathcal{C}_{jk} \frac{e^{-\kappa r}}{2\kappa r} \quad (69)$$

and

$$\mathcal{C}_{jk} = -\frac{1 - \kappa\sigma}{1 + \kappa\sigma} e^{2\kappa\sigma} \int_{\sigma}^{\infty} s e^{-\kappa s} c_{jk}^E(s) ds \quad (70)$$

Similarly, Eq. (34) can be integrated, leading to the following expression for $\delta h_{ij}^{(3)}(r)$

$$\delta h_{ij}^{(3)}(r) = \left(\frac{4\pi}{\epsilon}\beta\right)^2 e_i e_j \sum_{k,l} n_k e_k n_l e_l \mathcal{X}_{kl}(r) \quad (71)$$

with

$$\begin{aligned} \mathcal{X}_{kl}(r) &= \frac{e^{-\kappa r}}{4\kappa^2} \int_{\sigma}^r s e^{\kappa s} c_{kl}^E(s) ds - \frac{e^{\kappa r}}{4\kappa^2} \int_r^{\infty} s e^{-\kappa s} c_{kl}^E(s) ds \\ &\quad - \frac{e^{-\kappa r}}{4\kappa^2 r} \int_{\sigma}^r s^2 e^{\kappa s} c_{kl}^E(s) ds + \frac{e^{\kappa r}}{4\kappa^2 r} \int_r^{\infty} s^2 e^{-\kappa s} c_{kl}^E(s) ds \\ &\quad + \mathcal{C}_{kl} \frac{e^{-\kappa r}}{4\kappa^2} + \frac{1}{2\kappa^2} \Psi_{kl}(r) + \mathcal{D}_{kl} \frac{e^{-\kappa r}}{4\kappa r} \end{aligned} \quad (72)$$

and

$$\begin{aligned} \mathcal{D}_{kl} &= - \left[\frac{2\kappa\sigma^3}{(1 + \kappa\sigma)^2} \int_{\sigma}^{\infty} s e^{-\kappa s} c_{kl}^E(s) ds \right. \\ &\quad \left. + \frac{1 - \kappa\sigma}{\kappa(1 + \kappa\sigma)} \int_{\sigma}^{\infty} s^2 e^{-\kappa s} c_{kl}^E(s) ds \right] e^{2\kappa\sigma} \end{aligned} \quad (73)$$

C Thermodynamic integrations

In this appendix, more details are given on the simplifications used to perform the integrals involved in the thermodynamic quantities.

C.1 The internal energy

In order to facilitate the calculation of the various integrals encountered in ΔE , the boundary conditions introduced previously have been used. First, the differential equations (32) and (34) have been written more explicitly as

$$\frac{\partial^2 (r \Phi_j(r))}{\partial r^2} - \kappa^2 r \Phi_j(r) = \frac{4\pi}{\epsilon} \beta \sum_k n_k e_k r c_{jk}^E(r) \quad (74)$$

$$\frac{\partial^2 (r \delta h_{ij}^{(3)}(r))}{\partial r^2} - \kappa^2 r \delta h_{ij}^{(3)}(r) = \frac{4\pi}{\epsilon} \beta e_i e_j \sum_k n_k e_k r \Phi_k(r) \quad (75)$$

After integration between σ and ∞ , and taking into account the boundary conditions (66) and (67), it is obtained

$$\int_{\sigma}^{\infty} r \Phi_j(r) dr = -\frac{1}{\kappa^2} \left[\Phi_j(\sigma) + \frac{4\pi}{\epsilon} \beta \sum_k n_k e_k \int_{\sigma}^{\infty} r c_{jk}^E(r) dr \right] \quad (76)$$

$$\int_{\sigma}^{\infty} r \delta h_{ij}^{(3)}(r) dr = -\frac{1}{\kappa^2} \left[\delta h_{ij}^{(3)}(\sigma) + \frac{4\pi}{\epsilon} \beta e_i e_j \sum_k n_k e_k \int_{\sigma}^{\infty} r \Phi_k(r) dr \right] \quad (77)$$

These relations as been used to simplify the expression of ΔE . It has been found

$$\Delta E = -\frac{1}{2\beta} \sum_j n_j e_j \Phi_j(\sigma) - \frac{2\pi}{\epsilon \kappa^2} \sum_i n_i e_i \sum_j n_j e_j \delta h_{ij}^{(3)}(\sigma) \quad (78)$$

and using eq. (65) and (71), the eq. (37) for ΔE was obtained.

C.2 The Helmholtz free energy

The equation (39) used to calculate ΔA requires performing an integration according to λ of the function $F_{ij}(\lambda, r)$. This function is given by

$$\mathcal{F}_{ij}(\lambda, r) = \frac{\exp[-\lambda^{1/2} \kappa (r - \sigma)]}{1 + \lambda^{1/2} \kappa \sigma} \left(1 - \frac{\lambda^{1/2}}{2} \kappa r + \frac{\lambda \kappa^2 \sigma^2}{2(1 + \lambda^{1/2} \kappa \sigma)} \right) c_{ij}^E(\lambda, r) \quad (79)$$

If the excess direct correlation function $c_{ij}^E(r)$ is defined by Eq. (23), then

$$c_{ij}^E(\lambda, r) = \sum_{n=2}^{\infty} \frac{1}{n!} \left(\frac{-\lambda e_i e_j \beta}{\epsilon (1 + \lambda^{1/2} \kappa \sigma) r} \right)^n \exp[-n\lambda^{1/2} \kappa (r - \sigma)] \quad (80)$$

To make easier the integration, we used in place of λ the variable $u = \lambda^{1/2}$ and we expressed ΔA as a sum:

$$\Delta A = \sum_{n=2}^{\infty} \Delta A_n \quad (81)$$

with

$$\begin{aligned} \Delta A_n = & \frac{4\pi}{\epsilon n!} \sum_{i,j} n_i \epsilon_i^{n+1} n_j \epsilon_j^{n+1} \left(\frac{-\beta}{\epsilon} \right)^n \int_{\sigma}^{\infty} \frac{dr}{r^{n-1}} \cdot \\ & \int_0^1 du \frac{u^{2n+1}}{(1 + \kappa \sigma u)^{n+1}} \left(1 - \frac{\kappa r u}{2} + \frac{\kappa^2 \sigma^2 u^2}{2(1 + \kappa \sigma u)} \right) e^{-(n+1)\kappa(r-\sigma)u} \end{aligned} \quad (82)$$

Now using the relation:

$$\frac{\partial}{\partial u} \left[\frac{u^{2n+2}}{2(n+1)} \frac{e^{-(n+1)u\kappa(r-\sigma)}}{(1 + \kappa \sigma u)^{n+1}} \right] = u^{2n+1} \left[1 - \frac{\kappa r u}{2} + \frac{\kappa^2 \sigma^2 u^2}{2(1 + \kappa \sigma u)} \right] \frac{e^{-(n+1)u\kappa(r-\sigma)}}{(1 + \kappa \sigma u)^{n+1}} \quad (83)$$

The integration on the variable u can be performed analytically to give:

$$\Delta A_n = -\frac{2\pi}{\beta(n+1)!} \sum_{i,j} n_i n_j \int_{\sigma}^{\infty} \left(-\beta w_{ij}(r) \right)^{n+1} r^2 dr \quad (84)$$

Finally, by noting the similarity with the terms of the series expansion of $\exp[-\beta w_{ij}(r)]$, the expression (40) of ΔA was obtained.

C.3 The excess pressure

In this subsection, explicit expressions for the excess pressure asymmetry contribution are detailed. To facilitate the numerical evaluation of the various expressions obtained, the sums $(\sum_k n_k e^3)^2$ have been expressed as functions of κ^2 and of the parameter η_1 introduced by Onsager (see Eq. (10)). This allowed to rewrite the prefactor found in Eq. (44) and in the equations for the excess pressure, according to

$$\frac{\pi}{3} \left(\frac{\beta}{\epsilon(1 + \kappa \sigma)} \right)^3 \left(\sum_k n_k e^3 \right)^2 = \frac{1}{48\pi} \frac{\kappa^4}{(1 + \kappa \sigma)^3} \frac{\beta}{\epsilon} \eta_1^2 \quad (85)$$

It is noted that the ratio $\beta\eta_1^2/\epsilon$ has the dimension of a length.

First, from the equation (44) for the free energy $\beta\Delta A_2$, by differentiation according to the Eq. (47), the excess pressure $\beta\Delta P_2$ was obtained

$$\beta P_2 = \frac{1}{48\pi} \frac{\kappa^4}{(1 + \kappa\sigma)^3} \frac{\beta}{\epsilon} \eta_1^2 \left[e^{3\kappa\sigma} E_1(3\kappa\sigma) \left(1 + c_A \frac{\kappa^2\sigma^2}{(1 + \kappa\sigma)} \right) - \frac{1}{2} \right] \quad (86)$$

with the coefficient $c_A = 3/2$. The results of calculations carried out according to Eq. (86) are displayed in Fig. 1, for 2-1 or 3-1 electrolytes in water-like solvent at 25°C ($\epsilon_r = 78.3$). All the ions have the same diameter of 0.4 nm. For each type of salt, the contribution to the osmotic coefficient deduced by Debye and Hückel with volume excluded alone is compared with the sum of this contribution and the term $\beta P_2/n$. We observe for both salts that the additional contribution $\beta P_2/n$ induces an upward deviation at low concentrations and a downward deviation at high concentrations, compared to the contribution given by Debye and Hückel.

Alternatively, the excess pressure can be evaluated from the virial using the Eq. (50). Before evaluating the contribution of asymmetry it should be recalled that already for the term of reference deduced from the DH functions $h_{ij}^{\text{DH}}(r)$, the differentiation of the free energy and the use of the virial formula do not lead to the same result. If in Eq. (49), $\delta h_{ij}(r)$ is replaced by $h_{ij}^{\text{DH}}(r)$, the excess pressure $\beta\Delta P_1^v$ can be evaluated.

$$\beta\Delta P_1^v = -\frac{1}{24\pi} \frac{\kappa^3}{1 + \kappa\sigma}$$

This relation is known to give poorer results than that deduced from the free energy by differentiation. This comes from approximations used to obtain the Debye and Hückel correlation functions $h_{ij}^{\text{DH}}(r)$. then, for the corrective term $\delta h_{ij}(r)$ the comparison between the two paths to determine the excess pressure can also inform us about the robustness of the results obtained. From the Eq. (50), with $c_{ij}^{\text{E}}(r)$ given by the relation (24), the excess pressure $\beta\Delta P_2^v$ has been deducted

$$\beta\Delta P_2^v = \frac{1}{48\pi} \frac{\kappa^4\sigma}{(1 + \kappa\sigma)^2} + \frac{1}{3}\beta\Delta E_2 \quad (87)$$

where $\beta\Delta E_2/3$ was determined from the equation (36)

$$\frac{1}{3}\beta\Delta E_2 = \frac{1}{48\pi} \frac{\kappa^4}{(1 + \kappa\sigma)^3} \frac{\beta}{\epsilon} \eta_1^2 \left[e^{3\kappa\sigma} E_1(3\kappa\sigma) \left(1 + \frac{\kappa^2\sigma^2}{2(1 + \kappa\sigma)} \right) - \frac{1}{6} \right] \quad (88)$$

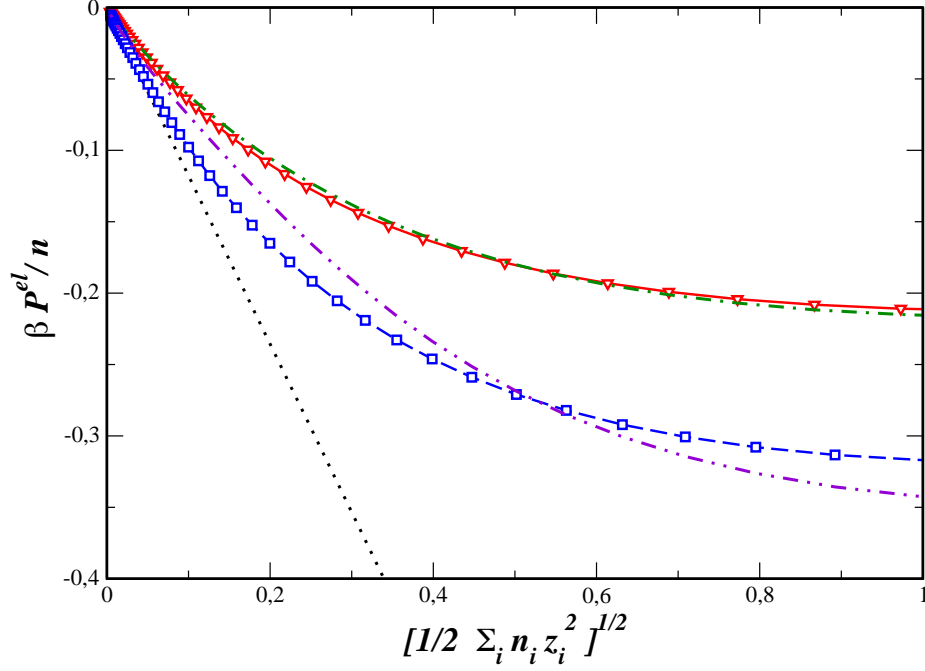


Figure 1: Electrostatic contributions $\beta P^{el}/n$ to the osmotic coefficient as a function of the square root of the ionic strength. Cations and anions have the same diameter $\sigma = 0.4$ nm. The two upper curves relate to a 2-1 electrolyte. The lower curves relate to a 3-1 electrolyte. Continuous red curve with triangles: DH contribution with excluded volume for a 2-1 electrolyte. Green curve in dashes and dots: Same contribution + $\beta P_2/n$ determined from Eq. (86). Blue curve with squares: DH contribution with excluded volume for a 3-1 electrolyte. Dashed and dotted purple curve: Same contribution + $\beta P_2/n$ determined from Eq. (86). Black dotted line: DH limiting law for a 3-1 electrolyte.

The first term in $\beta\Delta P_2^v$ gives a nonzero contribution for symmetric electrolytes. On the other hand, the second term $\beta\Delta E_2/3$, proportional to η_1^2 is specific to asymmetric electrolytes. When the first term in $\beta\Delta P_2^v$ is added to $\beta\Delta P_1^v$, the excess pressure calculated by Pitzer is obtained [50, 51]. The relation deduced by Pitzer is known to be a good correction of the expression $\beta\Delta P_1^v$.

If $\delta\Delta P_2^v$ contains a corrective term compared to $\beta\Delta P_1^v$, then it is possible that the following contribution $\beta\Delta P_3^v$ brings a correction to the asymmetric part deduced from $\beta\Delta P_2^v$. Indeed, the next term in the expansion of $c_{ij}^E(\sigma)$ from Eq. (23), (namely: $(-\beta w_{ij}(r))^3/6$), allows to determine with the first term of Eq. (50) a correction proportional to η_1^2 . In order to make comparisons with the asymmetric part $\beta\Delta P_2$, we can separate the expression of the excess pressure deduced from the virial into a symmetric contribution $\beta\Delta P_s^v$ and an asymmetric contribution $\beta\Delta P_a^v$. Shorter range terms are neglected here. The symmetrical contribution is that corresponding to the excess pressure calculated by Pitzer. The asymmetrical contribution is that deduced from the addition of second term of $\beta\Delta P_2^v$ and of the first term in $\beta\Delta P_3^v$.

$$\beta P_a^v = \frac{1}{48\pi} \frac{\kappa^4}{(1 + \kappa\sigma)^3} \frac{\beta}{\epsilon} \eta_1^2 \left[e^{3\kappa\sigma} \text{E}_1(3\kappa\sigma) \left(1 + c_v \frac{\kappa^2\sigma^2}{(1 + \kappa\sigma)} \right) - \frac{1}{2} \right] \quad (89)$$

with the coefficient $c_v = 1/2$. The comparison between $\beta\Delta P_2$ and $\beta\Delta P_a^v$ indicates that these two equations differ only by the coefficient c_A in (86), replaced by c_v in (89).

D Analysis according to the dressed ion theory

In this section, starting from the functions $\hat{h}_{ij}(q)$ deduced from the integral equations, a representation of the type of that of the DIT is obtained. This analysis brings an additional interpretation on the corrective terms, introduced by Onsager and recovered using the integral equations.

The approximation (23) was used to define the direct correlation functions $c_{ij}^E(r)$. This allowed to evaluate the corrective terms $\delta h_{ij}(r)$ from a first-order expansion of the excess integral equation (26). Implicitly, resolution limited to the first-order assumes that the corrective terms are small compared to the reference term. Since the corrective

terms are proportional to concentration, they are smaller at lower concentrations. If the corrective terms become too important the convergence of a calculation in perturbation is not ensured. To better describe the functions at the highest concentrations, it seems necessary to also study the higher order terms and to carry out a resummation of the expressions obtained.

Starting from the order zero for which $\hat{h}_{ij} \simeq \hat{h}_{ij}^0$, it was found that the additional terms to the first order are proportional to \hat{c}_{ij}^E . Later, the second-order supplementary terms are proportional to $(\hat{c}^E)^2$ and so on. All these corrections are products of functions \hat{h}^0 and functions \hat{c}^E . Moreover, it is observed in the set of corrective terms that any number of \hat{c}^E functions can succeed each other. This last characteristic can easily be deduced from Eq. (26). If we assume that all the functions $\hat{h}_{ik}^0 = 0$, in the equation (26) we obtain an OZ-like equation

$$\hat{h}_{ij} = \hat{c}_{ij}^E + \sum_k n_k \hat{c}_{ik}^E \cdot \hat{h}_{kj} \quad (90)$$

The functions which are solutions of these particular equations were denoted \hat{h}_{ij}^E . Evaluating in perturbation the solution of this equation we recover a sum of product of functions \hat{c}_{ij}^E

$$\hat{h}_{ij}^E \simeq \hat{c}_{ij}^E + \sum_k n_k \hat{c}_{ik}^E \left[\hat{c}_{kj}^E + \sum_l n_l \hat{c}_{kl}^E \left(\hat{c}_{lj}^E + \dots \right) \right]$$

In the perturbation expansion of (26), when this sum of products of functions \hat{c}_{ij}^E was found, it has been subsequently denoted \hat{h}_{ij}^E . On the other hand, in all of these corrective terms, it is observed within each series that two functions \hat{c}^E can only be separated by a single function \hat{h}^0 . Then, after considering all possible products of function \hat{c}^E , it is observed within each series that two functions \hat{h}^E can only be separated by a single function \hat{h}^0 .

Some corrections are series that start with a function \hat{h}_{ik}^0 and end with a function \hat{h}_{lj}^0 . For example, we find \hat{h}_{ij}^0 at zero order and at first order the product $n_k \hat{h}_{ik}^0 n_l \hat{c}_{kl}^E \hat{h}_{lj}^0$, which led to the term $\delta \hat{h}_{ij}^{(3)}$. The set of corrective terms presenting this characteristic has been

denoted \hat{h}_{ij}^{00} . The series of terms corresponding to $\hat{h}_{ij}^{00}(q)$ can be summed according to

$$\hat{h}_{ij}^{00}(q) = \hat{h}_{ij}^0(q) + \sum_k n_k \hat{h}_{ik}^0(q) \sum_l n_l \hat{h}_{kl}^E(q) \cdot \hat{h}_{lj}^{00}(q) \quad (91)$$

Using the functions $\hat{h}_{ij}^E(q)$ and $\hat{h}_{ij}^{00}(q)$, it was found that $\hat{h}_{ij}(q)$ can be separated into five terms according to

$$\begin{aligned} \hat{h}_{ij}(q) = \hat{h}_{ij}^E(q) + \hat{h}_{ij}^{00}(q) + \sum_k n_k \left[\hat{h}_{ik}^{00}(q) \hat{h}_{kj}^E(q) \right. \\ \left. + \hat{h}_{ik}^E(q) \left(\hat{h}_{kj}^{00}(q) + \sum_l n_l \hat{h}_{kl}^{00}(q) \hat{h}_{lj}^E(q) \right) \right] \quad (92) \end{aligned}$$

Using Eq. (19) for the functions $\hat{h}_{ij}^0(q)$, from Eq. (91), it was found that $\hat{h}_{ij}^{00}(q)$ can be rewritten as

$$\hat{h}_{ij}^{00}(q) = -\frac{4\pi}{\epsilon} \beta \frac{e_i e_j}{q^2 + \kappa_*^2} \quad (93)$$

with

$$\kappa_*^2 = \kappa^2 + \frac{4\pi}{\epsilon} \beta \sum_k n_k e_k \sum_l n_l e_l \hat{h}_{kl}^E(q) \quad (94)$$

Similarly, from Eq. (92), it was found that $\hat{h}_{ij}(q)$ can be rewritten as

$$\hat{h}_{ij}(q) = \hat{h}_{ij}^E(q) - \frac{4\pi}{\epsilon} \beta \frac{e_i^* e_j^*}{q^2 + \kappa_*^2} \quad (95)$$

with

$$e_i^* = e_i + \sum_k n_k e_k \hat{h}_{ik}^E(q) \quad (96)$$

Equivalently, the effective screening parameter κ_* can be defined from these effective charges

$$\kappa_*^2 = \frac{4\pi}{\epsilon} \beta \sum_k n_k e_k e_k^* \quad (97)$$

Considering the expansion at low concentrations of $\hat{h}_{ij}^{00}(q)$ from Eq. (91), by replacing $\hat{h}_{ij}^{00}(q)$ in the right side by $\hat{h}_{ij}^0(q)$, we recover that $\hat{h}_{ij}^{00}(q)$ looks like $\hat{h}_{ij}^0(q) + \delta \hat{h}_{ij}^{(3)}(q)$ as established in section 4, but with \hat{c}^E replaced by \hat{h}^E in this latter term. Since at low

concentrations \hat{h}^E tends towards \hat{c}^E , the expression of $\delta\hat{h}_{ij}^{(3)}(q)$ presented before is recovered in this limit. Equivalently, the expansion at low concentrations of $\hat{h}_{ij}^{00}(q)$ can be performed from Eq. (93). In the denominator, $q^2 + \kappa_*^2$ is replaced by $q^2 + \kappa^2 + \delta\kappa^2$. Here, $\delta\kappa^2$ represents the difference between κ_*^2 and κ^2 , given by Eq. (94). Expanding to first order in $\delta\kappa^2$, at low concentrations we recover again the terms $\hat{h}_{ij}^0(q)$ and $\delta\hat{h}_{ij}^{(3)}(q)$. Therefore, the term $\delta\hat{h}_{ij}^{(3)}(q)$ represents the effect of the variation of the screening parameter coming from the first-order consideration of the functions $\hat{c}_{ij}^E(q)$. Similarly, the terms included in $\delta\hat{h}_{ij}^{(2)}(q)$ represent corrections coming from the difference between the effective charges e_i^* and bare charges e_i .

Finally, if at low concentrations, it is assumed that $\hat{h}_{ij}^E(q) \simeq \hat{c}_{ij}^E(q)$, then Eqs. (51-53) can be deduced from Eqs. (95-97).

References

- [1] P. Debye, E. Hückel, Gefrierpunktserniedrigung und verwandte erscheinunge. Phys. Z. 24 (1923) 185-206.
- [2] The collected papers of Peter J. W. Debye (Interscience Publishers, Inc., New York, 1954), pp. 217, 264.
- [3] R. A. Robinson, R. H. Stokes, Electrolyte Solutions. , Butterworths London 1959.
- [4] B. Maribo-Mogensen, G. M. Kontogeorgis, K. Thomsen, Comparison of the Debye-Hückel and the mean spherical approximation theories for electrolyte solutions. Ind. Eng. Chem. Res. 51 (2012) 5353-5363.
- [5] G. M. Kontogeorgis, B. Maribo-Mogensen, K. Thomsen, The Debye-Hückel theory and its importance in modeling electrolyte solutions. Fluid Phase Equilibria 462 (2018) 130-152.
- [6] D. P. Zarubin, A. N. Pavlov, A closer look at the Debye-Hückel theory and its modification in the SiS model of electrolyte solutions. Mol. Phys. 118 (2020) e1685137.

- [7] R. Kjellander, A multiple decay-length extension of the Debye-Hückel theory: to achieve high accuracy also for concentrated solutions and explain under-screening in dilute symmetric electrolytes. *Phys. Chem. Chem. Phys.* 22 (2020) 23952-23985.
- [8] G. M. Silva, X. Liang, G. M. Kontogeorgis, Investigation of the limits of the linearized Poisson-Boltzmann equation. *J. Phys. Chem. B* 126 (2022) 4112-4131.
- [9] N. Bjerrum, Untersuchungen über Ionenassoziation. *Kgl. Dan. Vidensk. Selsk. Math. Fys. Medd.* 7 (1926) 1.
- [10] T. H. Gronwall, V. H. La Mer, K. Sandved, Über den einfluss der sogenannten höheren glieder in der Debye-Hückelschen theorie der lösungen starker elektrolyte. *Physik. Z.* 29 (1928) 358-393.
- [11] V. K. LaMer, C. F. Mason, Activity coefficients of electrolytes. II. The unsymmetric valence-type effect in highly dilute solutions. *J. Am. Chem. Soc.* 49 (1927) 410-426.
- [12] V. K. LaMer, T. H. Gronwall, L. J. Greiff, The influence of higher terms of the Debye-Hückel theory in the case of unsymmetric valence type electrolytes. *J. Phys. Chem.* 35 (1931) 2245-2288, E 3103-3104.
- [13] L. Onsager, A Correction to the Poisson-Boltzmann equation for unsymmetrical electrolytes. *J. Am. Chem. Soc.* 86, (1964) 3421-3423,
- [14] W. G. McMillan Jr., J. E. Mayer, The statistical thermodynamics of multicomponent systems. *J. Chem. Phys.* 13 (1945) 276-305.
- [15] J. E. Mayer, The theory of ionic solutions. *J. Chem. Phys.* 18 (1950) 1426-1436.
- [16] J. C. Rasaiah, H. Friedman, Integral equation methods in the computation of equilibrium properties of ionic solutions. *J. Chem. Phys.* 48 (1968) 2742-2752.
- [17] E. Waisman and J. L. Lebowitz, Exact solution of an integral equation for the structure of a primitive model of electrolytes. *J. Chem. Phys.* 52 (1970) 4307-4309;
- [18] E. Waisman and J. L. Lebowitz, Mean spherical model integral equation for charged hard spheres I. Method of solution. *J. Chem. Phys.* 56 (1972) 3086-3092.

- [19] E. Waisman and J. L. Lebowitz, Mean spherical model integral equation for charged hard spheres. II. Results. *J. Chem. Phys.* 56 (1972) 3093-3099.
- [20] L. Blum, Mean spherical model for asymmetric electrolytes I. Method of solution. *Mol. Phys.* 30 (1975) 1529-1535.
- [21] L. Blum and J. S. Høye, Mean spherical model for asymmetric electrolytes. 2. Thermodynamic properties and the pair correlation function. *J. Phys. Chem.* 81 (1977) 1311-1316.
- [22] K. Hiroike, Supplement to Blum's theory for asymmetric electrolytes. *Mol. Phys.* 33 (1977) 1195-1198.
- [23] J. M. J. Van Leeuwen, J. Groeneveld, J. de Boer, New method for the calculation of the pair correlation function. I. *Physica* 25 (1959) 792-808.
- [24] T. Morita and K. Hiroike, A New approach to the theory of classical fluids. I. *Progr. Theoret. Phys. (Kyoto)* 23 (1960) 1003-1027.
- [25] L. Verlet, On the theory of classical fluids. *Nuovo Cim.* 18 (1960) 77-101.
- [26] H. Friedman, A. Smitherman, R. De Santis, Models having the thermodynamic properties of aqueous alkaline earth halides and NaCl-MgCl₂ mixtures. *J. Sol. Chem.* 2 (1973) 59-81.
- [27] B. Hribar-Lee, V. Vlachy, Thermodynamic properties of charge asymmetric mixed electrolytes in the primitive model. *J. Mol. Liq.* 118 (2005) 163-169.
- [28] T. Mohorič, M. Lukšič, B. Hribar-Lee, Thermodynamics of asymmetric primitive model electrolytes via the hypernetted chain approximation. *Acta Chim. Slov.* 59 (2012) 490-502.
- [29] M. Gouy, Sur la constitution de la charge électrique à la surface d'un électrolyte. *J. Phys. Theor. Appl.* 9 (1910) 457-468.
- [30] D.L. Chapman, A contribution to the theory of electrocapillarity. *Phil. Mag.* 25 (1913) 475-481.

- [31] G. Stell and J. L. Lebowitz, Equilibrium properties of a system of charged particles. *J. Chem. Phys.* 48 (1968) 3706-3717.
- [32] E. Martina, F. Del Rio, Extended mean spherical approximation for electrolyte solutions. *Physica A* 86 (1977) 185-190.
- [33] M. Medina Noyola, D. A. McQuarrie, W. Olivares, On a class of extended mean spherical approximations. *Chem. Phys. Lett.* 58 (1978) 351-354.
- [34] D. Henderson, L. Blum, D. A. McQuarrie, W. Olivares, An extended mean spherical approximation calculation of the potential of an electrified interface. *Chem. Phys. Lett.* 71 (1980) 569-571.
- [35] D. J. Mitchell, B. W. Ninham, Range of the screened coulomb interaction in electrolytes and double layer problems. *Chem. Phys. Lett.* 53 (1978) 397-399.
- [36] M. A. Knackstedt, B. W. Ninham, Correlations and thermodynamic coefficients in dilute asymmetric electrolyte solutions. *J. Phys. Chem.* 100 (1996) 1330-1335.
- [37] H. Falkenhagen, W. Ebeling, Equilibrium properties of ionized dilute electrolytes. *Ionic Interactions From Dilute Solution to fused Salts.* Academic Press (1971), 1-59.
- [38] J. C. Rasaiah, Computations for higher valence electrolytes in the restricted primitive model. *J. Chem. Phys.* 56 (1972) 3071-3085.
- [39] H. L. Friedman, W. D. T. Dale, Electrolyte solutions at equilibrium. *Statistical Mechanics, Part A: Equilibrium Techniques*, (1977), 85-135.
- [40] E. Haga, On Mayer's theory of dilute ionic solutions. *J. Phys. Soc. Jpn.* 8 (1953) 714-723.
- [41] H. L. Friedman, C. V. Krishnan, Charge-asymmetric mixtures of electrolytes at low ionic strength. *J. Phys. Chem.* 78 (1974) 1927-1932.
- [42] J. P. Valleau, L. K. Cohen, D. N. Card, Primitive model electrolytes. II. The symmetrical electrolyte. *J. Chem. Phys.* 72 (1980) 5942-5954.

- [43] W. Ebeling, Zur theorie der Bjerrumschen ionenassoziation in elektrolyten. *Z. Physik. Chem.* 238 (1968) 400-402.
- [44] H. Yokayama, H. Yamatera, A theory of ion association as a complement of the Debye-Hückel theory. *Bull. Chem. Soc. Japan* 48 (1975) 1770-1776.
- [45] W. Ebeling, M. Grigo, An analytical calculation of the equation of state and the critical point in a dense classical fluid of charged hard spheres. *Ann. Physik.* 492 (1980) 21-30.
- [46] Y. Zhou, S. Yeh, G. Stell, Criticality of charged systems. I. The restricted primitive model. *J. Chem. Phys.* 102 (1995) 5785-5795.
- [47] S. Yeh, Y. Zhou, G. Stell, Phase separation of ionic fluids: An extended Ebeling-Grigo approach. *J. Phys. Chem.* 100 (1996) 1415-1419.
- [48] K. S. Pitzer, Thermodynamics of electrolytes. I. Theoretical basis and general equation. *J. Phys. Chem.* 77 (1973) 268-277.
- [49] K. S. Pitzer, Electrolyte theory - Improvements since Debye and Hückel. *Acc. Chem. Res.* 10 (1977) 371-377.
- [50] R. Kjellander, D. J. Mitchell, An exact but linear and Poisson-Boltzmann-like theory for electrolytes and colloid dispersions in the primitive model. *Chem. Phys. Lett.* 200 (1992) 76-82.
- [51] R. Kjellander, D. J. Mitchell, Dressed ion theory for electrolyte solutions: a Debye-Hückel-like reformulation of the exact theory for the primitive model. *J. Chem. Phys.* 101 (1994) 603626.
- [52] R. Kjellander, J. Ulander, Effective ionic charges, permittivity and screening length: dressed ion theory applied to 1:2 electrolyte solutions. *Mol. Phys.* 95 (1998) 495-505.
- [53] J. Ulander, R. Kjellander, Screening and asymptotic decay of pair distributions in asymmetric electrolytes. *J. Chem. Phys.* 109 (1998) 9508-9522.

- [54] A. McBride, M. Kohonen, P. Attard, The screening length of charge-asymmetric electrolytes: A hypernetted chain calculation. *J. Chem. Phys.* 109 (1998) 2423-2428.
- [55] F. H. Stillinger Jr., R. Lovett, Ion-pair theory of concentrated electrolytes. I. Basic concepts. *J. Chem. Phys.* 48 (1968) 3858-3868.
- [56] F. H. Stillinger Jr., R. Lovett, General restriction on the distribution of ions in electrolytes. *J. Chem. Phys.* 49 (1968) 1991-1994.
- [57] C. W. Outhwaite, Comment on the second moment condition of Stillinger and Lovett. *Chem. Phys. Lett.* 24 (1974) 73-74.
- [58] T. J. Murphy, E. G. D. Cohen, Corrections to the FuossOnsager theory of electrolytes. *J. Chem. Phys.* 53 (1970) 2173-2186.