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To cite this version:

O. Bernard. Association in electrolyte solution: Implementing inner sphere ion pairing into the mean spherical approximation. Journal of Molecular Liquids, 2023, 390, pp.123023. 10.1016/j.molliq.2023.123023 . hal-04503560

Association in electrolyte solution: Implementing inner sphere ion pairing into the mean spherical approximation.

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Keywords: Electrolytes, Thermodynamic properties, Association.

Abstract

In many electrolyte solutions, ions of opposite signs can be paired due to electrostatic or more specific interactions. The pairing may occur in competition with the individual solvation of the ions. Some of the solvent molecules, initially present around each of the ions, may be excluded between pairing ions. The resulting complexes can be seen as dumbbells with a strong overlap between the spheres representing each of the hydrated ions involved in the association. The thermodynamic description of electrolyte solutions containing such pairing ions is described in this paper with a variational generalisation of the binding mean spherical approximation.

1 Introduction

Debye and Hückel (DH) theory continues to play a vital role in the interpretation of the thermodynamic properties of electrolytes at low concentration [1–3]. It provided a justification for the variations in square root of the concentration observed for several experimental quantities in highly dilute solutions of strong electrolytes. In the concentration range where this limiting law is relevant, the ions can be characterized only by their charge to describe solution properties. In this model, the solvent is seen as a continuum surrounding the ions and characterized by its dielectric constant. At high concentration, a size must be assigned to the ions. This induces deviations from the limiting law and allows one to account for the variation of the thermodynamic and transport properties of dissociated electrolytes. In the DH theory, the size of the ions was introduced as a short-range boundary condition in the determination of the average electrostatic potential around the ions. Indeed, the screening length characterizing the range of this electrostatic potential does not depend on the size of the ions. This implies a limitation in the field of application of the DH theory. In order to provide a more satisfactory description of the properties at higher concentrations, many further developments have been made. In particular, the mean spherical approximation theory (MSA) constitutes an extension of DH [4–9]. It provides also an analytical description of several properties such as activity and osmotic coefficients. It better takes into account the effect of the size of the ions on their distributions in space and on the screening length in concentrated solutions.

In applications, the size parameters of the ions are most often ajusted by fitting properties, such as the osmotic coefficients, is described as best as possible by the theoretical expressions adopted. This approach is particularly satisfactory in the case of alkali halides in aqueous solution [10–15]. Furthermore, the sizes of the ions in solution determined in this way are usually greater than the crystallographic sizes. This difference is generally ascribed to the fact that ions in solution can have strong short-range interactions with water molecules that induce the formation of a solvation layer around them. The dimensions of the ions thus determined are representative of hydrated species and delineate the region beyond which the solvent can be seen as a continuum.

Solvation and hydration are observed in microscopic measurements such as dielectric spectroscopy, low-frequency Raman spectra or NMR relaxation [16–23]. Furthermore, in order to account for thermodynamic quantities such as compressibility or hydration heat capacity, it is often assumed that a firm layer of water molecules is present around the ions. These hydration layer are assumed to have properties different from free bulk water molecules. Hydration can also be highlighted in the structure factors of the ions in neutron or X-ray diffraction measurements or from radial distribution functions obtained from numerical simulations. When the solvation energy is high, the layers of water surrounding the ions repel each other at short distances. This feature appears to be particularly outstanding when the distance of least approach between cations and anions can be greater than the sum of their respective crystallographic radii. In this situation, it seems more relevant to consider hydrated sizes to characterize ions in solution.

Furthermore, to better describe the properties of electrolytes, association between unlike ions must be taken into consideration. When such ions are attracted towards each other, at short distance this attraction competes with the interaction with the solvent molecules surrounding each of the ions. If the solvation energy is large enough, the attraction between ions fails to break their hydration layers. When association occurs between strongly solvated ions, the ions in contact retain their respective solvation layers. Then, to provide a simple picture of this situation, the anion-cation pair can be represented as a dumbbell consisting of two spheres bound together.

However, the competition between solvation and association does not necessarily leave the hydration layers unchanged. This may be due to the fact that the individual solvation energy of some ions is weaker than the attraction by counter-ions, as a result of electrostatic or more specific interactions, which can possibly lead to a true chemical bond. This overlapping of the solvation layers during association has been considered to interpret various experimental data from Raman spectroscopy, dielectric relaxation, ionic conductivity or sound absorption [24–38]. Different configurations of associated ions have been considered. In addition to ion pairs separated by solvent, ion pairs with shared solvent (with one water molecule between ions) and pairs in contact (without any water molecules between the two ions) have been taken into account to describe the dielectric relaxation or the absorption of sound in the electrolyte. Different association constants are assigned to these three types of configuration. Alternatively, the pairing ions were sometimes split into inner-sphere and outer-sphere complexes, with no distinction between contact and solvent-shared paired ions. Moreover the competing effects of solvation and association led to the formulation of the law of matching water affinities which states that ions of opposite charge are more likely to form inner sphere ion pairs when they have equal water affinities [39]. Additionally, hydration layers can also be strongly modified during an acid-base reaction. A hydronium ion can be considered as bulky when dissociated, due to its solvation. When forming an inner sphere complex with an anion a significant part of their hydration layers can be released.

To calculate the proportions of the various constituents, several association constants have been defined, depending on whether the solvation layers overlap between the paired ions. Moreover, in order to describe the deviations from ideality in the thermodynamics of the solutions, it is advisable to take into account the geometric shapes specific to each of the complexes assumed to be present in the medium.

Previously simple forms of complexes have been used in the literature. First, due to its simplicity, the anion-cation pair was modeled as a sphere. This representation has been used by different groups [40–47]. The radius of the spherical complex is an additional parameter in this model. During the association process of two ions, if one of them penetrates deep into the hydration layer of the other, it can replace one or more solvent molecules in its solvation shell. The complex formed can then be considered as roughly spherical. This situation is assumed to relate to contact association.

As an alternative, the anion-cation pair can be represented as a dumbbell consisting of the two spheres bound together. This picture may represent complexes formed by two spherical ions retaining their respective solvation layers. The corresponding thermodynamic properties can be described by using the associative or binding MSA (AMSA or BiMSA) theory [48–52]. This paper is dedicated to Myroslav Holovko, a well-known expert in statistical mechanics, especially in integral equation theories. He is one of the founders of the AMSA or BiMSA theory.

Finally, it is desirable to describe complexes having an intermediate structure between these two configurations. Various models of the thermodynamic contributions due to these dimers, similar to dumbbells having a overlapping of spheres, have been presented for uncharged hard spheres [53–61]. The influence of the charges carried by these objects has been less studied [62–67]. It should be noted that the AMSA approximation has been applied to the fluid of charged hard spheres having a bonding distance less than the size of the hard spheres [64]. However, the description of the thermodynamics is not as explicit as when the bond occurs at the contact distance. Then, in this work, an approximate description of the electrostatic contributions is presented to account for dimers having a overlapping of spheres when they are charged. Different thermodynamic formalisms have been used previously to describe association in solution. Some have been referred to as chemical models, when they explicitly consider paired solutes as a third species. Others ascribe the pairing from very directional attractive interactions and are said to come from a physical framework. Many studies have presented relationships between these two formalisms [67–74]. These relations are used here more explicitly to describe ionic solutions within the framework of MSA theory. They are also generalized to describe ion pairs of intermediate geometries. As a starting point, for simplicity it was assumed that in a binary electrolyte the dissociated anions and cations have the same diameter. Previously, this simple model with a single size parameter for a given salt, led to a satisfactory description of dissociated electrolytes in water. In this article, only one type of ion pair was considered at a time. The two extreme geometries, namely the spherical and dumbbell-like complexes without overlapping, are reviewed first. A common formalism is presented in order to highlight the common features and the differences in the thermodynamic expressions related to the charges carried by the various constituents present. The use of a common formalism makes it possible to take into account subsequently several types of complexes simultaneously. Then alternative thermodynamic expressions are established to describe ion pairs having intermediate configurations. Extensions, called variational MSA, of MSA type models have been set up before [75–77]. This approach was established previously to consider ions having non-spherical shapes such as ellipsoids. This theoretical tool has been used here to represent dumbbell-shaped charged complexes. As a result, the theoretical expressions obtained interpolate between MSA relations for spherical ions and those from BiMSA in which the complexes are dumbbells without overlap.

2 Thermodynamic and association for two particular configurations

Before presenting the method used to establish the thermodynamics of an electrolyte forming dimers, with overlapping of the spheres representing the cation and the anion, two particular configurations can be recalled.

- The first is that obtained when the larger of the two spheres completely covers the other. Then, the dimer is a sphere of the same size as the larger ion and the electrolyte is made up of a mixture of charged hard spheres. The MSA theory seems suitable to describe this case.
- The second case is one in which the two ions are in contact without overlap. It is the largest distance between the two constituents of the pair that will be considered in this study. This configuration is the one previously described by the BiMSA theory.

These two configurations represent bounds to the equations determined subsequently for configurations comprised in between. However, these two extreme configurations have been described within different theoretical frameworks. In order to be able to pass continuously from one configuration to another it is necessary to determine how to describe intermediate complexes in a unique theoretical framework. The chemical model, initially used to describe spherical ion pairs, is recalled first. In this model the complex is seen as a third charged species which is added to the two free ions. It has been named a three-solute (3S) model. In particular the free energy is split into ideal and excess parts. The ideal contribution applies to a mixture of three different species.

In contrast, the BiMSA theory was established within the framework of thermodynamic perturbation theory (TPT) and Wertheim's integral equations [50, 51]. There is no mention of free ions. The ideal free energy describes the mixture of two species only by not distinguishing free and bound ions. To distinguish it from the previous one, this approach has sometimes been called a physical model.

Each of the thermodynamic frameworks is presented first, without presupposing the geometry of the complexes for which each framework has been chosen as most appropriate. Then, explicit expressions adapted to a given complex geometry are given.

2.1 Thermodynamic framework of the chemical model

2.1.1 General relations

In the most compact configuration, where the pair is a sphere, the mixture of free ions and dimers is most simply described by considering three charged species, denoted with the indices $1, 2$ and 3. The species 1 and 2 are the two free ions

$$\begin{aligned}\rho_1 =&\rho_{_C}\alpha_{_C}\\ \rho_2 =&\rho_{_A}\alpha_{_A}\end{aligned} \tag{1}$$

where $\rho_{_C}$ and $\rho_{_A}$, denote the total number densities of species C and A, and where $\alpha_{_C}$ and $\alpha_{_A}$ are the fractions of free C and A, respectively. The third particle is the pair such that $\rho_3 = \rho_{_P}$. Conservation of the total quantities of C and A requires

$$\begin{aligned}\rho_{_C} =&\rho_1 + \rho_3\\ \rho_{_A} =&\rho_2 + \rho_3\end{aligned} \tag{2}$$

For this mixture of three solutes, the Helmholtz free energy $F_{_{3S}}$ is split into two terms according

$$\beta F_{_{3S}} = \beta F_{_{3S}}^{id} + \beta F_{_{3S}}^{ex} \tag{3}$$

where $\beta F_{_{3S}}^{id}$ is the free energy of the ideal mixture given by

$$\beta F_{_{3S}}^{id} = \sum_{i=1}^{3} \rho_i \Big(\beta\mu_i^o + \ln\rho_i - 1\Big) \tag{4}$$

and $\beta F_{_{3S}}^{ex}$ is the excess contribution due to interactions in solution. Since the three constituents are charged spheres, these excess terms can be described taking into account a hard sphere contribution βF_{3S}^{HS} and an electrostatic contribution like that of the MSA theory βF_{3S}^{MSA}.

$$\beta F_{3S}^{ex} = \beta F_{3S}^{HS} + \beta F_{3S}^{el} \tag{5}$$

The 3S subscript indicates a mixture of 3 species.

The chemical potential μ_i of a constituent can be determined by differentiation of the free energy,

$$\begin{aligned} \beta\mu_i &= \left(\frac{\partial \beta F_{3S}}{\partial \rho_i}\right)_{\rho_{k\neq i}} \\ &= \beta\mu_i^o + \ln \rho_i + \beta\mu_i^{ex} \end{aligned} \tag{6}$$

where the excess part $\beta\mu_i^{ex}$ of the chemical potential can be written using γ_i, the individual activity coefficient of the constituent i

$$\beta\mu_i^{ex} = \ln \gamma_i \tag{7}$$

Moreover, the chemical equilibrium condition between the free ions and the pair may be written as

$$\mu_1 + \mu_2 = \mu_3 \tag{8}$$

In addition, the Helmholtz free energy F_{3S} must also represent the thermodynamics of the solution by considering only the two total densities ρ_A and ρ_C. Indeed these densities are the real variables known experimentally. If, on the one hand, the chemical species noted here 1, 2 and 3 can have a real existence, on the other hand they may only serve to better take into account attractive interactions at short distance (physical framework). In particular, this latter point of view can be put forward when the association is only due to short-range electrostatic interactions, as in the approach of Bjerrum. In this situation ion pairs do not necessarily have a long lifetime and are used to more properly describe the short-range presence probabilities between anions and cations. Consequently, whether one chooses to use a chemical model, or a more physical description of the type presented in the following subsection, the calculated free energy must be the same for given total densities ρ_A and ρ_C.

Accordingly, the quantities ρ_1, ρ_2 and ρ_3 are seen as functions of $\rho_{_A}$ and $\rho_{_C}$. Then, the chemical potentials $\mu_{_A}$ and $\mu_{_C}$ are determined by differentiation with respect to $\rho_{_A}$ or $\rho_{_C}$ respectively, taking into account the conservation of the total quantities of A and C. Using the relationship

$$\frac{\beta F_{_{3S}}}{\partial \rho_{_M}} = \sum_{k=1}^{3} \frac{\beta F_{_{3S}}}{\partial \rho_k} \, \frac{\partial \rho_k}{\partial \rho_{_M}} \tag{9}$$

for $M = A$ or C. (In summations or enumerations, to avoid confusion with densities of free and bound ions presented previously, capital letters are used for subscripts relating to total densities). Then, by using also the conservation of A and C given by eq. (2), it is found that

$$\beta\mu_{_C} = \frac{\partial \beta F_{_{3S}}}{\partial \rho_{_C}} = \beta\mu_1 + \Big(\beta\mu_3 - \beta\mu_1 - \beta\mu_2\Big) \, \frac{\partial \rho_3}{\partial \rho_{_C}} \tag{10a}$$

$$\beta\mu_{_A} = \frac{\partial \beta F_{_{3S}}}{\partial \rho_{_A}} = \beta\mu_2 + \Big(\beta\mu_3 - \beta\mu_1 - \beta\mu_2\Big) \, \frac{\partial \rho_3}{\partial \rho_{_A}} \tag{10b}$$

If the condition (8) of chemical equilibrium between the free ions and the pair is fulfilled, the term in brackets in the previous equations is zero, then it is not necessary to evaluate the terms proportional to $\partial\rho_3/\partial\rho_{_C}$ or $\partial\rho_3/\partial\rho_{_A}$. So, it is deduced that $\mu_{_C} = \mu_1$. Similarly it is found that $\mu_{_A} = \mu_2$ [67, 69].

Moreover, eq. (8) is equivalent to the following chemical equilibrium relation

$$K_p^o = \frac{\rho_3}{\rho_1 \rho_2} \, \frac{\gamma_3}{\gamma_1 \gamma_2} \tag{11}$$

where the association constant K_p^o is related to the standard chemical potential μ_i^o of the three constituents by

$$K_p^o = \exp\left[\beta\mu_1^o + \beta\mu_2^o - \beta\mu_3^o\right] \tag{12}$$

2.1.2 Application to the spherical dimers

As said before, these relations are directly applicable to the association model in which the ion pair is represented by a sphere. In this situation, the excess free energy $F_{_{3S}}^{ex}$ is the sum of two contributions, according to eq. (5). These two contributions, βF_{3S}^{HS} and βF_{3S}^{MSA}, are both functions of the three densities ρ_1, ρ_2 and ρ_3. The hard sphere contribution can be evaluated using the expressions given in [78,79], when the three species have different diameters. When the ions all have the same diameter the expressions given in [80] are recovered,

$$\beta F_{3S}^{HS} = \rho \, \frac{4\phi - 3\phi^2}{(1-\phi)^2} \tag{13}$$

where $\rho = \rho_1 + \rho_2 + \rho_3$ and $\phi = (\pi/6)\rho\sigma^3$.

In the same way the electrostatic term is also a function of the three densities. The charge of the third species is $z_3 = z_1 + z_2$. From the MSA theory, the electrostatic free energy term is given by

$$\beta F_{3S}^{el} = \beta F_{3S}^{MSA} = \beta E_{3S}^{MSA} + \frac{\Gamma^3}{3\pi} \tag{14}$$

where βE_{3S}^{MSA} is the internal energy which is given by

$$\beta E_{3S}^{MSA} = -\lambda \sum_{k=1}^{3} \rho_k \, \frac{\Gamma z_k^2}{1 + \Gamma\sigma} \tag{15}$$

We used the notation

$$\lambda = \frac{\beta e^2}{4\pi\varepsilon_o\varepsilon_r} \tag{16}$$

for the Bjerrum distance, with $\beta = 1/k_B T$ (k_B being the Boltzmann constant and T the temperature), e is the elementary charge, ε_o is the permitivity of a vacuum, and ε_r is the dielectric constant of pure solvent. The MSA parameter Γ is given by

$$\Gamma^2 = \pi\lambda \sum_{k=1}^{3} \rho_k \, \frac{z_k^2}{(1 + \Gamma\sigma)^2} \tag{17}$$

By differentiation the electrostatic contribution to the activity coefficient $\ln\gamma_i$ of ions i is deduced

$$\ln\gamma_i^{MSA} = -\lambda \frac{\Gamma z_i^2}{1 + \Gamma\sigma} \tag{18}$$

2.2 The physical thermodynamic framework

2.2.1 General relations

The thermodynamic description of stretched dimers has been established by considering only two species, namely the monomers A and C, which are able to bond together due to highly directional attractive interactions. In particular, for uncharged species the Helmoltz free energy has been obtained using the Wertheim's thermodynamic perturbation theory (TPT) [81–84]. The AMSA or BiMSA theories, based on integral equations, have provided a means of evaluating additional electrostatic contributions [51,52]. In the physical framework, the thermodynamic quantities are not described with the densities of the three previous species but rather with $\rho_{_A}$ and $\rho_{_C}$. As before, the Helmholtz free energy F_{2S} is split into two terms [86]

$$\beta F_{_{2S}} = \beta F^{id}_{_{2S}} + \beta F^{ex}_{_{2S}} \tag{19}$$

where $\beta F^{id}_{_{2S}}$ is the free energy of the ideal mixture given by

$$\beta F^{id}_{_{2S}} = \rho_{_A}\Big(\beta\mu^o_{_A} + \ln\rho_{_A} - 1\Big) + \rho_{_C}\Big(\beta\mu^o_{_C} + \ln\rho_{_C} - 1\Big) \tag{20}$$

and $\beta F^{ex}_{_{2S}}$ is the excess contribution due to interactions in solution. As an alternative, in the physical thermodynamic framework, the excess free energy is split into three contributions

$$\beta F^{ex}_{_{2S}} = \beta F^{_{HS}}_{_{2S}} + \beta F^{ass}_{_{2S}} + \beta F^{el}_{_{2S}} \tag{21}$$

As before, a hard spheres term $\beta F^{_{HS}}_{_{2S}}$ and an electrostatic term $\beta F^{el}_{_{2S}}$ are used. The hard sphere contribution can be evaluated using the equations coming from [78], namely by using (13) with $\phi = (\pi/6)\rho_t\sigma^3$, which is now a function of the two densities $\rho_{_A}$ and $\rho_{_C}$ because $\rho_t = \rho_{_A} + \rho_{_C}$. An associative term $\beta F^{ass}_{_{2S}}$, reflecting the effect of association, has been added. In addition, the concentration of ion pairs $\rho_{_P} = \rho_3$ appears in both the associative and electrostatic terms, as a result of attractive interactions. The associative contribution $F^{ass}_{_{2S}}$ to the free energy is given by [83]

$$\beta F^{ass}_{_{2S}} = \sum_{M=A}^{C} \rho_{_M}\left(\ln\alpha_{_M} + \frac{1}{2}\left(1-\alpha_{_M}\right)\right) \tag{22a}$$

$$= \rho_{_A}\ln\alpha_{_A} + \rho_{_C}\ln\alpha_{_C} + \rho_{_P} \tag{22b}$$

where the fractions of free ions are defined in eq. (1).

2.2.2 Application to dumbbell-shaped dimers

These relations are directly applicable to the association model in which the ion pair is represented by two spheres bonded together. Additionally for this geometry, to specify the assessment of attractive interactions, the concentration of ion pairs $\rho_{_P}$ is now defined by

$$\rho_p = \rho_{_C} \alpha_{_C} \rho_{_A} \alpha_{_A} K_p \tag{23}$$

where the term K_p is related to $g_{_{CA}}(\sigma)$ the pair distribution function at contact between C and A [83]

$$K_p = K_p^o \, g_{_{CA}}(\sigma) \tag{24}$$

When the species C and A are not charged, $g_{_{CA}}(\sigma)$ only involves a contribution due to the hard spheres $g_{_{CA}}^{_{HS}}(\sigma)$, for which explicit expressions are given in [78, 79]. When the constituents of the pair are charged, the pair distribution function $g_{_{CA}}(\sigma_{_{CA}})$, used in equation (24), contains an extra electrostatic contribution. In this case, this function was defined by [51, 85]

$$g_{_{CA}}(\sigma) = g_{_{CA}}^{_{HS}}(\sigma) \; \exp\left[-\beta W_{_{CA}}^{el}\right] \tag{25}$$

where the electrostatic energy $W_{_{CA}}^{el}$ was given in the BiMSA by

$$\beta W_{_{CA}}^{el} = \frac{\lambda}{\sigma} \left[\frac{z_{_C} \; z_{_A}}{(1 + \Gamma^B \sigma)^2} - z_{_C} \; z_{_A} \right] \tag{26}$$

The presence of the electrostatic term $\beta W_{_{CA}}^{el}$ in the function $g_{_{CA}}(\sigma)$ affects the associative contribution to chemical potentials. By differentiation it is found

$$\frac{\partial \beta F_{_{2S}}^{ass}}{\partial \rho_{_M}} = \ln \alpha_{_M} - \rho_p \frac{\partial \ln g_{_{CA}}^{_{HS}}(\sigma)}{\partial \rho_{_M}} + \rho_p \frac{\partial \beta W_{_{CA}}^{el}}{\partial \rho_{_M}} \tag{27}$$

for $M = A$ or C. The first two terms are those obtained for uncharged hard spheres with TPT [83]. The last term is another electrostatic contribution which complements those deduced from the differentiation of $\beta F_{_{2S}}^{el}$.

For ions of different diameters, the expression of the electrostatic contribution to the free energy βF_{2S}^{el}, can be found in [51, 85–87]. In order not to make this development unnecessarily cumbersome, only the relations usable when the ions have the same diameter are now given. In this case, the term βF_{2S}^{el} was given by BiMSA, as follows

$$\beta F_{2S}^{el} = \beta F_{2S}^{BiMSA} = \beta E^{el0} + \frac{\left[\Gamma^B\right]^3}{3\pi} \tag{28}$$

The internal energy E^{el} used to obtain F_{2S}^{el} includes two contributions

$$\beta E^{el} = \beta E_0^{el} + \beta E_1^{el} \tag{29}$$

The term E_0^{el}, is similar to the usual expression for the internal energy in the MSA (without association) but in which the parameter Γ is replaced by the new parameter Γ^B defined below in eq. (33).

$$\beta E_0^{el} = -\lambda \left[\rho_C z_C \, \frac{\Gamma^B z_C}{1+\Gamma^B\sigma} + \rho_A z_A \, \frac{\Gamma^B z_A}{1+\Gamma^B\sigma}\right] \tag{30}$$

The second contribution βE_1^{el}, is the one due to anion-cation association. When the ions have the same diameter, βE_1^{el} is related to βW_{CA}^{el}, defined in eq. (26), by the simple relation

$$\beta E_1^{el} = \rho_p \, \beta W_{CA}^{el} \tag{31}$$

When the diameters of the ions are different, the contribution βE_1^{el} is not exactly equal to $\rho_p \, \beta W_{CA}^{el}$. Additional terms were found in the expressions of βF_{2S}^{BiMSA} [51]. Nevertheless it is important to present the two contributions of the internal energy. Indeed, the free energy was obtained by a charging process from the internal energy. If part of the latter is omitted, the deduced free energy will be modified. Moreover, the following general relation between the internal energy and the parameter Γ^B was found [50]

$$\left(\frac{\partial \beta E^{el}}{\partial \Gamma^B}\right)_{\rho_p} = -\frac{\left[\Gamma^B\right]^2}{\pi} \tag{32}$$

Accordingly, the parameter Γ^B is defined by

$$\left[\Gamma^B\right]^2 = \pi\lambda \left[\, \rho_C \frac{z_C^2}{\left(1+\Gamma^B\sigma\right)^2} + \rho_A \frac{z_A^2}{\left(1+\Gamma^B\sigma\right)^2} + 2\,\rho_p \, \frac{z_C \; z_A}{\left(1+\Gamma^B\sigma\right)^3}\right] \tag{33}$$

Thereafter, the relation (32) is used in the variational extensions of the MSA theory.

In the physical framework the determination of the chemical potentials $\mu_{_A}$ and $\mu_{_C}$, by differentiation of the free energy, appears to be more tedious. However, by summing the derivatives of $\beta F^{ass}_{_{2S}}$ and $\beta F^{BiMSA}_{_{2S}}$ with respect to the parameter Γ^B, it was found that

$$\frac{\partial F_{_{2S}}}{\partial \Gamma^B} = 0 \tag{34}$$

Consequently, this relation allows one to calculate the derivatives of the free energy with respect to the densities while keeping the parameter Γ^B constant. This enables us to determine the electrostatic part of the individual activity coefficients $ln\gamma^{el}_{_M}$ of ions M as

$$\ln \gamma^{el}_{_M} = -\lambda \frac{\Gamma^B z^2_{_M}}{1 + \Gamma^B \sigma} \tag{35}$$

which is similar to the activity coefficient expression (18) obtained with the MSA, but with the parameter Γ^B instead of Γ.

2.3 Transition between the two representations

From this point several improvements are possible. First, it is described below how to allow simultaneously for the two geometries of ion pairing. However either the chemical or the physical model is used for one or the other geometry. So, it is necessary to be able to describe all pairing configurations with a single approach. Previously, relations were established to describe dumbbell-like pairs within the chemical model framework [86]. In this framework, the chemical potential of the paired ions is explicitly defined. This enabled one to modify the size of the constituents of the complex without changing those of the free ions. Relations allowing the transition between the two frameworks are now taken up. First of all, the equivalence between the two theoretical frameworks is necessary to impose that the free energy $F_{_{2S}}$ is equal to $F_{_{3S}}$. By comparing these two expressions for the free energy it is found that

$$\beta F^{id}_{_{3S}} = \beta F^{id}_{_{2S}} + \beta F^{ass} + \rho_p \, \ln \left(\frac{\gamma_1 \gamma_2}{\gamma_3} \right) \tag{36}$$

Furthermore, to be in agreement with the relation (11), the function $g_{CA}(\sigma)$ must be related to the ratio of the activity coefficients according to

$$\ln g_{CA}(\sigma) = \ln\left(\frac{\gamma_1\gamma_2}{\gamma_3}\right) \tag{37}$$

This relation is necessary to establish a connection between the two thermodynamic frameworks. It is obvious in the physical representation. It is not necessarily emphasised in the chemical description, which simply defines the activity coefficient of the ion pair. Then, the free energy of solutions containing dumbbell-shaped dimers can be rewritten within the framework of the chemical model, from eq.(36), according to

$$\beta F_{2S} = \beta F^{id}_{3S} + \beta F^{HS}_{2S} + \beta F^{el}_{2S} - \rho_p \ \ln g_{CA}(\sigma) \tag{38}$$

In addition, the electrostatic contribution to the chemical potential of dumbbell-shaped dimers can be deduced from eqs. (35) and (37)

$$\ln\gamma^{el}_3 = \ln\gamma^{el}_A + \ln\gamma^{el}_C + \beta W^{el}_{CA}(\sigma) \tag{39}$$

Besides, when the dimers are considered as spherical, as seen before, this shape can result from the complete integration of the smaller ion into the bigger one. In this configuration the distance between the two ions can be taken equal to zero. The formula (37), relating the ratios of activity coefficients to the pair distribution function, can be generalized for distances l, between the two ions, lower than the minimum distance of approach σ.

$$\ln\gamma_3 = \ln(\gamma_1\gamma_2) - \ln y_{CA}(l) \tag{40}$$

In this relation the pair distribution function has been replaced by the background or cavity correlation function $y_{CA}(l)$. This function can be seen as an analytic continuation, at distances less than σ, of the pair distribution function. It is connected to the latter and to the interaction potential $V_{CA}(l)$ by the following relationship: $g_{CA}(l) = y_{CA}(l)\exp -\beta V_{CA}(l)$. For $l = \sigma$, $y_{CA}(\sigma) = g_{CA}(\sigma)$. In continuity with the relation (25), this function can also be splitted into two contributions according to

$$\ln y_{CA}(l) = \ln y^{HS}_{CA}(l) - \beta W^{el}_{CA}(l) \tag{41}$$

For uncharged species, the description of the association for distances $l \leq \sigma$ has been studied. Explicit formulas for calculating the function $y^{HS}_{CA}(l)$ have been established [88,89]. The electrostatic part is less well known. Various expressions describing $W^{el}_{CA}(l)$ are presented in the next section.

When $l = 0$ the function $\ln y_{CA}(l)$ can be determined explicitly from the various contributions to the logarithms of the activity coefficients, as they have been described in the part relating to the chemical model. In particular, when $l = 0$, the electrostatic contribution to the function $y_{CA}(0)$ can be calculated from the activity coefficients given in eq. (18). It is obtained

$$\ln \gamma_3^{MSA} = \ln \gamma_1^{MSA} + \ln \gamma_2^{MSA} - \lambda \frac{2\Gamma\, z_A z_C}{1 + \Gamma\sigma} \tag{42}$$

As an alternative, by using eqs.(40), (41) and (42), the following expression for the function $W^{el}_{CA}(0)$ has been found within the MSA

$$\beta W^{el}_{CA}(0) = -\lambda \frac{2\Gamma\, z_A z_C}{1 + \Gamma\sigma} \tag{43}$$

In the next section, an extension of the relations with a single diameter but with overlapping binding ions is presented.

3 Generalisation with overlapping ions in a dimer

Eq. (40) allows one to define the activity coefficient of the pair from those of the free ions and the background correlation function. It was seen in the previous section that this relation is applicable for the two extreme configurations of the pairing ions. Moreover, in view of eq. (18) and (35), the free ion activity coefficients are described by almost the same relationship for both configurations. The two equations differ only through the parameter Γ in (18), being replaced by Γ^B in (35). As a first step, it is assumed that the activity coefficients of free ions can be described with the same type of relation, when the pairing ions are separated by a distance l that is such that $0 \leq l \leq \sigma$.

$$\ln \gamma^{el}_M = -\lambda \frac{\Gamma^v z_M^2}{1 + \Gamma^v \sigma} \tag{44}$$

where the parameter Γ^v is given by a relation of the same type as equations defining the parameters Γ and Γ^B. This relationship can be determined using eq. (32). Then, having defined the activity coefficients of the free ions, it remains to determine the term $\ln y_{CA}(l)$ in eq. (40) to evaluate $\ln \gamma_p$.

3.1 Closure relation for $\ln y_{CA}(l)$

From eq. (41), the function $\ln y_{CA}(l)$ is split into a hard sphere and an electrostatic term. The hard spheres contribution of this function was previously described very correctly [88,89]. So, in this study only the term $\beta W^{el}_{CA}(l)$ was evaluated. Various closure relations have been used to relate pair correlation functions to interaction potentials. In particular for electrolytes, the MSA and the hypernetted chain (HNC) approximations are suitable. Due to the presence of an exponential connecting $g_{CA}(\sigma)$ to the potential $W^{el}_{CA}(\sigma)$ in eq. (25), the HNC relation has been preferred to obtain an expression for $W^{el}_{CA}(l)$. The HNC relation is given by [90–92]

$$\ln g_{CA}(l) = -\beta V_{CA}(l) + h_{CA}(l) - c_{CA}(l) \tag{45}$$

The cavity correlation function $y_{CA}(l)$ is related to $g_{CA}(l)$ and to the interaction potential $V_{CA}(l)$ by the relation

$$\ln g_{CA}(l) = -\beta V_{CA}(l) + \ln y_{CA}(l) \tag{46}$$

which allows us to deduce $y_{CA}(l)$ from the HNC relation. If only the electrostatic part of $\ln y_{CA}(l)$ is determined with the HNC closure, then only the corresponding parts of $h_{CA}(l) - c_{CA}(l)$ are needed. With this restriction, the relation adopted is therefore

$$\ln y^{el}_{CA}(l) = -\beta W^{el}_{CA}(l) = h^{el}_{CA}(l) - c^{el}_{CA}(l) \tag{47}$$

Then expressions for the functions h^{el}_{CA} and c^{el}_{CA} are needed. Previously, they were determined in the BiMSA theory by using Wertheim integral equations. In particular, when $l = \sigma$, the electrostatic part of the total correlation functionis given by

$$h^{el}_{CA}(\sigma) = -\lambda \frac{z_A z_C}{\sigma \left(1 + \Gamma^B \sigma\right)^2} \tag{48}$$

and the direct correlation function $c^{el}_{CA}(\sigma) = -\lambda z_A z_C/\sigma$. Then, eq. (47) is suitable to retrieve eq. (26). For distances $l < \sigma$, $h^{el}_{CA}(l) = 0$. Therefore in this range of distance, eq. (47) reduces to

$$\ln y^{el}_{CA}(l < \sigma) = -c^{el}_{CA}(l) \tag{49}$$

Equivalently, from the HNC relation, the activity coefficient of pairing ions is given by

$$\ln \gamma^{el}_{P} = \ln \gamma^{el}_{A} + \ln \gamma^{el}_{C} + c^{el}_{CA}(l) \tag{50}$$

where the activity coefficients of the free ions are given by eq. (44).

In order to apply these relations, analytical MSA expressions were used to evaluate the direct correlation functions $c^{el}_{CA}(l)$ [9, 93]. For ions of the same diameter, it has been found

$$\ln y^{el}_{CA}(l \leq \sigma) = \lambda \frac{\Gamma^v z_A z_C}{(1+\Gamma^v \sigma)^2}\Big[2 + \Gamma^v (2\sigma - l)\Big] \tag{51}$$

In addition, the parameter Γ, initially present in the MSA formula, has been replaced by Γ^v. Moreover, the strict inequality: $l < \sigma$, has been replaced by $l \leq \sigma$, because there is continuity of the function $h_{CA} - c_{CA}$ in the MSA approximation at $l = \sigma$.

3.2 Variational extension of the MSA theory

The parameter Γ^v was determined using the variational generalization of MSA thermodynamics [75–77]. Application of this method is now described. One of the common properties of MSA and BiMSA is that the electrostatic free energy F^{el} is related to E^{el} by the relation

$$\beta F^{el} = \beta E^{el} + \frac{[\Gamma^v]^3}{3\pi} \tag{52}$$

Here too, the parameter Γ^v is used to designate both the MSA parameter, the BiMSA parameter and more generally the screening parameter corresponding to an intermediate geometry. Another common property of MSA and BiMSA given by eq. (32) is generalized as follows

$$\left[\frac{\partial \beta E^{el}}{\partial \Gamma^v}\right]_{\rho_p} = -\frac{[\Gamma^v]^2}{\pi} \tag{53}$$

With this relation the electrostatic part of the individual activity coefficients $\gamma_{_M}^{el}$ of the ions M can be obtained by differentiation of the internal electrostatic energy E^{el} according to

$$\ln \gamma_{_M}^{el} = \left(\frac{\partial \beta E^{el}}{\partial \rho_{_M}} \right)_{\Gamma^v, \rho_p} \tag{54}$$

The internal energy E^{el} is the sum of the following two contributions

$$\beta E_0^{el} = -\lambda \left[\rho_{_C} z_{_C} \frac{\Gamma^v z_{_C}}{1 + \Gamma^v \sigma} + \rho_{_A} z_{_A} \frac{\Gamma^v z_{_A}}{1 + \Gamma^v \sigma} \right] \tag{55}$$

$$\beta E_1^{el} = \rho_p \beta W_{_{CA}}^{el}(l) = -\lambda \rho_{_P} \frac{\Gamma^v z_{_C} z_{_A}}{(1 + \Gamma^v \sigma)^2} \left[2 + 2\Gamma^v \sigma - \Gamma^v \, l \right] \tag{56}$$

Then Γ^v is deduced, by differentiating βE^{el} with respect to Γ^v, which yields

$$\begin{aligned} [\Gamma^v]^2 = \pi \lambda \Bigg[& \rho_{_C} \frac{z_{_C}^2}{(1 + \Gamma^v \sigma)^2} + \rho_{_A} \frac{z_{_A}^2}{(1 + \Gamma^v \sigma)^2} \\ & + 2 \, \rho_{_P} \frac{z_{_C} z_{_A}}{(1 + \Gamma^v \sigma)^3} \Big(1 + \Gamma^v (\sigma \ - l) \Big) \Bigg] \end{aligned} \tag{57}$$

This relation completes the description of the free energy model for a binary electrolyte when association leads to ion pairs with overlapping spheres. As with the boundary configurations used previously, the equations can be solved iteratively. For example, from relation (11), giving the ratio of bound ions to free ions, neglecting initially the activity coefficients, the concentrations of free and bound ions can be calculated. Then, the parameter Γ^v can then be determined with these concentrations for a given distance l. The activity coefficients can be evaluated. The ratio of these coefficients can be taken into account in relation (11) and the concentrations of free and bound ions can be calculated again. These equations are thus solved iteratively until there are no significant differences between the concentrations determined between two successive iterations. Then, the chemical potential of the pair 3 is equal to the sum of the chemical potentials of the ions 1 and 2. When this relation is satisfied, $\beta\mu_{_C} = \beta\mu_1$ and $\beta\mu_{_A} = \beta\mu_2$.

4 Discussion

Use has been made of the background correlation function to define the thermodynamics of electrolytes when overlapping occurs between pairing ions. In this study, this function has been used to represent the variation of the probability that two ions have to be at a distance less than σ_{CA}. The use of the direct correlation function from MSA in the HNC relation has allowed to establish explicit expressions of the electrostatic part of the cavity correlation function for ions all having the same diameter. These expressions recover the explicit formulas previously established in the MSA for spherical pairs on the one hand and for two spheres in contact with the BiMSA on the other hand. In view of eqs. (49) and (50), $\ln \gamma_{P}^{el}(l)$ and $\ln y_{CA}^{el}(l)$ are linear functions of the distance l between the paired ions.

Based on previous works, this linear variation can be easily found. In order to determine the cavity correlation function, Zhou and Stell assumed that this function could be represented by an interpolation polynomial between two states. By applying this hypothesis to the electrostatic contribution of the cavity function, the potential $W_{CA}^{el}(l)$ can be represented by the following relation

$$\beta W_{CA}^{el}(l) = \beta W_{CA}^{el}(0)\ (1-x) + \beta W_{CA}^{el}(\sigma)\, x \tag{58}$$

where $W_{CA}^{el}(0)$ and $W_{CA}^{el}(\sigma)$ are given by (43) and (26), respectively, and $x = l/\sigma$. This definition restores eq. (47) deduced from the HNC relation, and eq. (57) for Γ^{v} using the variational scheme presented previously. The use of an interpolation polynomial is simpler. However the HNC relation has more physical basis.

From the theoretical expressions presented in the previous section, the logarithm of the mean activity coefficient $\ln \gamma_{\pm}$ of a 1-1 electrolyte solution in a water-like solvent at 25^{o}C ($\varepsilon_r = 78.3$) has been evaluated. The cations and anions in the electrolyte were assumed to have the same diameter $\sigma = 4\,\mathrm{nm}$. In order to highlight the influence of the association, increasing values of the association constant were considered. The association constant $\mathcal{K}_p^{o}$, was assumed to be equal to: 0, 0.5 or 1 M^{-1} (where M denotes molarity). The distance l, between the components of the complex, was supposed equal to: zero, half or one σ diameter, to display the influence of its geometry. The results of these calculations are shown in Fig. 1. A comparison of the mean activity coefficients obtained with association and without association shows that the higher the association constant, the greater the decrease in this quantity. Furthermore, for a given association constant, below 0.5 M, the curves obtained with different distances are almost identical. On the other hand, at higher concentrations the activity coefficient $\ln \gamma_{\pm}$ is higher as the distance l tends towards σ. Then, it seems important to characterize the geometry of the complexes at high concentrations.

To go further, one can ask whether the approach developed so far for ions of the same size can still be used when their diameters are different. Starting from the MSA theory, a simplified expression of the ion activity coefficient is given by

$$\ln \gamma_i^{el} \simeq -\lambda \frac{\Gamma^v z_i^2}{1+\Gamma^v \sigma_i} \tag{59}$$

where the parameter Γ^v is equal either to Γ when only spheres are present in solution, or to Γ^B when the paired ions are in the form of stretched dumbbells. Moreover, the interaction energy $W_{CA}^{el}(\sigma_{CA})$ between two ions at the distance $\sigma_{CA} = (\sigma_A + \sigma_C)/2$ is given by

$$\beta W_{CA}^{el}(\sigma_{CA}) \simeq \frac{2\lambda}{(\sigma_A + \sigma_C)} \left[\frac{z_A z_C}{(1+\Gamma^B \sigma_A)(1+\Gamma^B \sigma_C)} - z_A z_C \right] \tag{60}$$

which is also a generalization of the equation (26) defined previously for ions having the same size.

On the other hand, assuming that $\sigma_A \geq \sigma_C$, the ion pairs are spherical when $l \leq s_{AC}$, with: $s_{AC} = (\sigma_A - \sigma_C)/2$. In this limit, the pairing ions still have a total charge $z_3 = z_A + z_C$, and a diameter equal to σ_A. In order to determine the function $W_{CA}^{el}(l = s_{AC})$, it is necessary to subtract from the excess chemical potential of the pairing ions the excess chemical potentials of the free ions. By using eq. (59) to calculate the electrostatic contributions to these chemical potentials, it is obtained instead of eq. (43),

$$\beta W_{CA}^{el}(s_{AC}) = -\lambda \frac{2\Gamma z_A z_C}{1+\Gamma \sigma_A} - \lambda \frac{\Gamma z_C^2}{1+\Gamma \sigma_A} + \lambda \frac{\Gamma z_C^2}{1+\Gamma \sigma_C} \tag{61}$$

The first term, proportional to $z_A z_C$, is a generalization of relation (43). The other terms, proportional to z_C^2, are new. They come from the fact that the C ions do not have the same size when they are free or bound.

In order to describe intermediate configurations, such as $s_{AC} \leq l \leq \sigma_{CA}$, the HNC relation can be used again to determine the term proportional to $z_A z_C$, namely: $\ln y_{CA}^{el}(l \leq \sigma_{CA}) =$

$-\beta W^{el}_{CA}(l \leq \sigma_{CA}) \simeq -c^{el}_{CA}(l)$. Then, to use eqs. (50) and (51), the direct correlation function $c^{el}_{CA}(l)$ can be deduced from the MSA equations [9, 93]

$$c^{el}_{CA}(l) = -\lambda \frac{\Gamma^v z_A z_C}{(1+\Gamma^v \sigma_A)\,(1+\Gamma^v \sigma_C)} \left[2 + \Gamma^v \Big(2\sigma_{CA} - L(l) \Big) \right] \tag{62}$$

where the function $L(l)$ is given by

$$L(l) = l + \frac{(\sigma_A - \sigma_C)^2}{4\,l} \tag{63}$$

These relations allow a generalization of eq. (51).

On the other hand, there are no terms proportional to z_C^2 in eq. (62) for $c^{el}_{CA}(l)$, in order to recover the corresponding terms present in (61) when $l = s_{AC}$. The HNC relation therefore seems insufficient to account for these terms obtained when the diameters of the ions are different. An interpolation polynomial could be used again to represent this contribution, which is absent in the HNC relation. To simplify the notation, the terms proportional to z_C^2 in eq. (61) can be named $W^{el}_{CC}(s_{AC})$, according to

$$\beta W^{el}_{CC}(s_{AC}) = -\lambda \frac{\Gamma^v z_C^2}{1+\Gamma^v \sigma_A} + \lambda \frac{\Gamma^v z_C^2}{1+\Gamma^v \sigma_C} \tag{64}$$

So, to account for the change in this contribution as a function of the distance l, a simple linear interpolation may be assumed, for $s_{AC} \leq l \leq \sigma_{CA}$,

$$\beta W^{el}_{CC}(l) = \beta W^{el}_{CC}(s_{AC})\ \ (1-x) \tag{65}$$

with $x = (l - s_{AC})/\sigma_C$. This function is zero when $l = \sigma_{CA}$.

Other interpolation schemes are possible. In particular, it can be noted that the function $c^{el}_{CA}(l)$ is no longer a linear function of l but rather depends on $L(l)$ when the ions have different sizes. This variable allows one to consider the point $l = s_{AC}$ as an extremum of the function $c^{el}_{CA}(l)$. Then it can be assumed that $W_{CC}(l)$ also depends on $L(l)$. If the function $L(l)$ is selected to define an interpolation polynomial, the change in $W^{el}_{CC}(l)$, can be represented alternatively by

$$\beta W^{el}_{CC}(l) = \beta W^{el}_{CC}(s_{AC})\ \Delta P_{AC}(l) \tag{66}$$

with

$$\Delta P_{AC}(l) = \frac{1}{2\sigma_C^2}\left[\sigma_A^2 + \sigma_C^2 - (\sigma_A + \sigma_C)\ L(l)\right] \tag{67}$$

This function is proportional to the overlapping surface of the two spheres. It is involved in the description of the background correlation functions of hard spheres. Then, as before, from a definition of the function $W_{CA}(l)$, the internal energy $E_1^{el} = \rho_P W_{CA}(l)$ can be made explicit. By using eq. (53), the screening parameter Γ^v can be obtained by differentiation of the internal energy. At this point the description of the thermodynamics for associated ions of different diameters is limited to being only a mathematical problem.

5 Conclusion

The consideration of charged dimers, in the form of dumbbells with overlapping spheres, has been undertaken in the continuity of the MSA theory. The connection between various association models has been reviewed. This can facilitate the consideration of several types of complexes simultaneously. Starting from simple geometries studied previously, dimers with a distance $0 \leq l \leq \sigma$ have been considered. As a generalisation, the cavity correlation function was used to represent the probability variation in these intermediate geometries. The HNC relation was used to define a relation between this function and the electrostatic part of the direct correlation function deduced from the MSA theory. The deduced expressions, give back the explicit formulas previously obtained in the MSA for spherical pairs on the one hand and for two spheres in contact with the BiMSA on the other hand. A variational generalisation of the binding mean spherical approximation was used to establish an explicit expression for the screening parameter Γ^v, which is required to evaluate the activity coefficients when the pairing ions are squeezed dumbbell shaped. In most sections of this study, the ions were assumed to have the same diameter. The approach used in this work could be extended for ions of different sizes. Further theoretical modeling, including numerical simulations, of solutions containing such pairing ions would be necessary to improve understanding of association in electrolytes.

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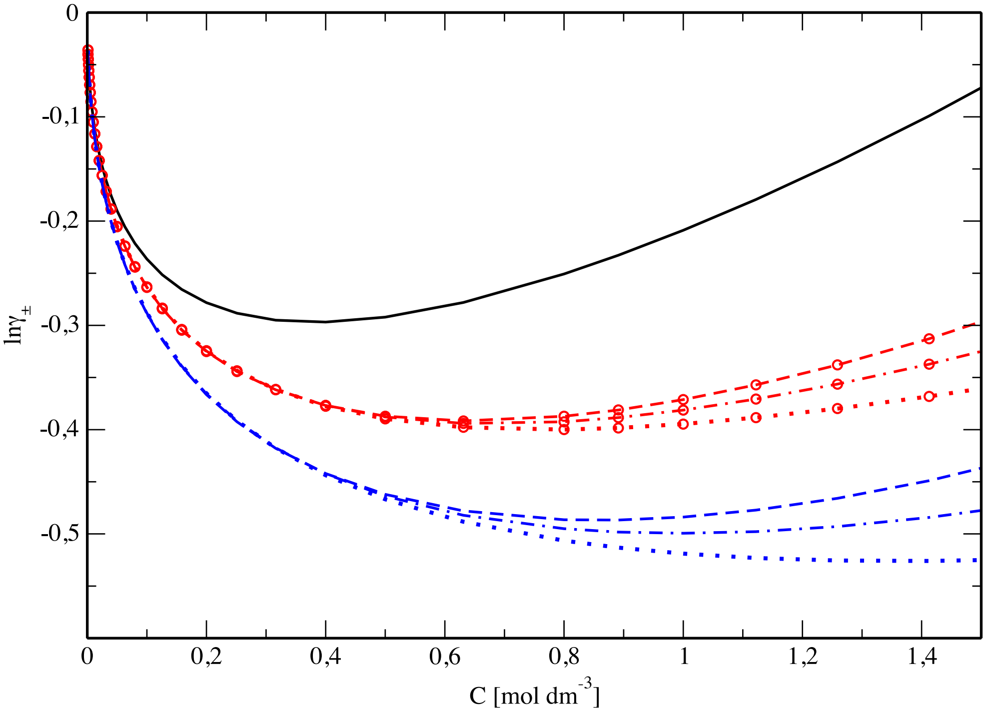

Figure 1: Mean activity coefficient for a 1-1 electrolyte as a function of the molar concentration C. Cations and anions have the same diameter $\sigma = 0.4$ nm. From top to bottom: The black continuous curve represents the result obtained with the MSA theory without association. The three red curves with circles represent the result obtained when a constant of association $\mathcal{K}_p^o = 0.5$ M^{-1} between cations and anions is taken into account. The three lower blue curves were calculated considering an association constant $\mathcal{K}_p^o = 1$ M^{-1}. For each of these two groups of three curves, the upper curve with dashes is determined with $l = \sigma$, the one with dashes and dots corresponds to $l = 0.5\,\sigma$ and the lowest with dots is $l = 0$.