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Further reflections about the “Born” term used in thermodynamic models for electrolytes

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Abstract

This paper is a follow-up of previous work about the “Born” term, which must not be confused with the famous Born equation for ion solvation energy. The “Born” term is an empirical formula that is often introduced in explicit-solvent models for electrolytes in conjunction with a contribution for ion-ion interactions taken from a model with implicit solvent. An inconsistency is found for the expression commonly used in the literature. The “Born” term is supposed to describe the effect of ion-solvent interactions. The relevance of the “Born” term for that purpose is further investigated by considering various different situations: The transfer of an ion from pure water into a pure molten salt is examined; then, the nonprimitive mean spherical approximation theory for mixtures of ions and dipoles (MSA-ID) is used to get further insight in the case of a waterlike solvent and, besides, in the limit of low density and low coupling where the MSA becomes exact. The various situations considered in this work further indicate that this term is unsuitable. The possibility of deriving a formula in the spirit of the original Born equation is also considered.

Keywords: “Born” term, electrolytes, non-primitive, ion-dipole, mean-spherical approximation (MSA).

1. Introduction

The so-called “Born” term has been employed extensively in the literature about the modeling of the thermodynamic properties of electrolytes, since it was proposed in 1978 by Cruz and Renon [1]. Hereafter quotes are used when mentioning it because Born was not the author of this formula. The “Born” term must not be confused with the famous Born equation for the solvation energy of an ion [2]. It has often been presented in the chemical engineering literature as following naturally from the latter, but this is not so as will be seen below.

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It has been used mainly in models with explicit solvent to describe the change in Gibbs energy when an ion is passed from a pure solvent (reference state at infinite dilution) to an ionic solution of finite salt concentration in the *same* solvent, generally water. Since the initial work of Cruz and Renon, the “Born” term has been employed in a wealth of thermodynamic models for electrolytes as, e.g., in Refs. 3–18 just to cite a few.

There are a priori two main issues associated with this contribution, which may be described as follows. Firstly, in these *explicit-solvent* models, it has played the role of accounting for ion-solvent interactions (as claimed, e.g., in Refs. 4, 16, 17) and, as such, it has been used in conjunction with a term for ion-ion interactions that was either a Debye-Hückel (DH) or a mean spherical approximation (MSA) term, both of which being theories regarding the solvent as a *dielectric continuum*. The latter feature contrasts with the type of models (with explicit-solvent) in which the “Born” term is usually employed. Secondly, the formula for the “Born” term was directly copied from the famous Born equation [2] for the Gibbs solvation energy of an ion, in which a lone ion is placed in a continuous solvent. The formula was written down by assimilating an ionic solution to a dielectric continuum of dielectric constant ϵ_{sol} (which quantity, by the way, is relevant for the description of interionic forces at large separations). This is a crude assumption, that by no means results from the Born equation for ion solvation. In this respect, the “Born” term is an empirical formula.

A discussion was proposed by this author in a recent publication [19] that questioned the relevance of the “Born” term. It is of paramount importance for the modeling of the thermodynamic properties of electrolytes to clearly assess the value of this contribution. If the “Born” term is indeed unsuitable, then it constitutes a major drag for the development of reliable models. Indeed, it introduces an invariably positive contribution of large magnitude, which may exaggerate the importance of this term as compared to other contributions. Furthermore, its lack of flexibility may strongly unbalance the resulting overall model. The aim of this work is to further investigate the relevance of the “Born” term.

In a very recent publication [20], the capability of the “Born” term was investigated using Monte Carlo simulations for the system NaCl+water. This is the first fundamental study dedicated to this issue since the publication of Ref. 19. An involved procedure was used in that valuable work [20] in order to attempt disentangling the various contributions to the mean salt chemical potential. However, because of uncertainties on the simulation results, and in the estimation of the ion-ion (MSA) contribution, it seems difficult to draw a clear and definitive conclusion about the suitability of the “Born” term from this study.

The present paper is organized as follows. After an introduction, and a presentation of the Born equation and the “Born” term, it is divided in several sections, each of which touching on a different significant and hopefully insightful problem in relation with the “Born” term. For convenience and clarity of the exposition, each section contains its own theoretical developments, results, and a discussion thereof. This organization was chosen because each of these problems could not be the subject of a full paper per se.

In the next section, the difference between the original Born equation [2] and the “Born” term is underscored. Then, the view that the “Born” term reflects the effect of ion-solvent interactions is scrutinized. For that purpose, an extreme case is considered first, in which an ion is transferred from pure water into a pure molten salt. Then, the solvation energy of an ion in a dilute electrolyte is calculated along the lines of Born’s seminal paper. After that, the nonprimitive mean spherical approximation theory for mixtures of ions and dipoles (MSA-ID) [21–23] is utilized to get further insight into the role that the “Born” term is supposed to play in explicit-solvent models. Former results about a dilute electrolyte in a waterlike solvent are first reexpressed in a more explicit and clearer way. Unlike previous work, the classical “Born” term, usually employed in chemical engineering models, is now calculated within the MSA-ID. The formalism allows one to build a relevant framework for the purpose intended by the “Born” term, namely a suitable contribution in an explicit-solvent model. Some results are given in the semi-restricted (cation and anion of the same size) and unrestricted (general) case for alkali chlorides. Next, the solution to the MSA-ID is obtained in the case of a mixture of ions and dipoles at low concentration of both components and high temperature (dilute plasma). In this limit of low density and low coupling, the MSA becomes exact, as shown in Appendix B. Hence, in this limiting case, the performance of the “Born” term can be tested in a rigorous manner. Finally, the main results of this work are summarized and some prospects are presented in the Conclusion.

2. The Born equation vs. the “Born” term

2.1. The Born equation for the solvation energy

Hereafter, ε_0 will designate the permittivity of a vacuum. The solvent will be water, with dielectric constant ε_W . The charge of a proton is e , the Boltzmann constant is denoted by k_B , the temperature by T , and $\beta = 1/k_B T$. The diameters of an ion i and of the water molecules (both modeled as hard spheres) will be σ_i and σ_W , respectively.

The case of a monovalent salt will be considered in what follows.

The famous original equation published by Born [2] involved a calculation of the energy of the electrostatic field created by a lone ion in a solvent regarded as a dielectric continuum of relative permittivity ε_W .

This energy was obtained by Born by summing the energy density $dW_i/d\tau$ in the continuum dielectric surrounding ion i . With $dW_i/d\tau = 1/2 \mathbf{D}\cdot\mathbf{E}$ where \mathbf{D} ($= \varepsilon_0\varepsilon_W \mathbf{E}$) and \mathbf{E} are the displacement vector and the electric field in the volume $d\tau$, respectively, he obtained,

$$W_i = \frac{1}{2} \varepsilon_0\varepsilon_W \int_{\sigma_i/2}^{\infty} E^2 d\tau \quad (1)$$

where $d\tau = 4\pi r^2 dr$, $E = e/4\pi\varepsilon_0\varepsilon_W r^2$, and the integration is performed from the surface of the ion at $r = \sigma_i/2$. Upon integration, the result for the energy of the electric field in the dielectric may be written in compact form as,

$$\beta W_i = \frac{L_0}{\sigma_i} \frac{1}{\varepsilon_W} \quad \text{with} \quad L_0 = \beta e^2/4\pi\varepsilon_0 \quad (2)$$

in units of $k_B T$, with $L_0 \simeq 560.4 \text{ \AA}$ at 25°C , and ε_0 the permittivity of a vacuum. The energy W_i is also the work required to charge the ion in the dielectric continuum.

Then, Born considered the transfer of an ion from a vacuum to pure water, and identified the corresponding variation in electrostatic energy with the hydration Gibbs energy of the ion, μ_i^{Hydr} , from Eq. (2), which yielded,

$$\beta \mu_i^{Hydr} = -\frac{L_0}{\sigma_i} \left(1 - \frac{1}{\varepsilon_W} \right) \quad (3)$$

This is the equation proposed by Born in 1920 [2]. Hereafter it will be mentioned as the Born equation (without quotes). It has been very successful for a first description of ion hydration energies, as well as for a first quantitative modeling of ionic solutions in terms of atomic parameters [24]. It has also been the subject of much discussion and debate [25–27]. In passing, it is noted that Ref. 25 proposes a contrasting and enlightening way of deriving the Born equation, in which ‘the work of discharging a monovalent ion in a vacuum and the work of recharging it after its immersion in the dielectric are zero’.

An important progress was made when an expression was derived from an *explicit-solvent* model within the non-primitive MSA-ID in which the water molecule is represented as a hard dipole [28, 29]. At infinite dilution of the salt, the ion-dipole contribution in the MSA-ID, μ_i^{id} , is the Gibbs solvation energy of ion i (the reference state in MSA-ID is a system that is infinitely dilute in ions and dipoles). Remarkably, it turns out that it has the following expression [19, 28, 29],

$$\beta \mu_i^{Hydr} = -\frac{L_0}{\sigma_i + \sigma_W/\lambda} \left(1 - \frac{1}{\varepsilon_W} \right) \quad (4)$$

which has strong resemblance to the Born equation [Eq. (3)], but includes an additional distance, σ_W/λ , where λ is a polarization parameter for the solvent (see also Section 5.1 below) that has a value of ~ 2.65 for a waterlike solvent in ambient conditions [19]. This extra distance is a consequence of the granularity of the solvent and dielectric saturation in the vicinity of the ion, which is accounted for in the MSA-ID model, but not in Born theory. Eq. (4) provides a justification for this long-known [30] distance that must be added to the ion diameter in the Born equation for recovering experimental data [31]. It was also found [19] that it gives results that are quite in keeping with experimental data when Shannon and Prewitt crystallographic diameters are used for the ions.

It must be noticed that dipole-dipole interactions play a role in the Gibbs solvation energy. This more subtle effect, which arises from the creation of a cavity in the solvent in order to accommodate the ion, was studied within the MSA-ID by Garisto et al. [32] and later by Fawcett and Blum [33]. Nevertheless, since this effect is generally small, it will be neglected in what follows.

Let us mention finally that it is clear that a suitable contribution of the Born type must indeed be employed when a lone ion is transferred from one solvent to another, as occurs in the modeling of solute partitioning between immiscible solvents. In that case, the interactions of the ion with its environment are modified, and this term accounts for the variation of solvation of the ion between the two solvents. It represents the change in the reference chemical potential of an ion i , μ_i^0 . For this purpose, the Born equation, or its MSA-ID counterpart [Eq. (4)], may be used.

2.2. The “Born” term

2.2.1. Basic assumptions

This term has often been introduced in models for electrolyte solutions as a contribution to the change in the chemical potential of an ion in the process depicted in Figure 1. In this process, a lone ion in a solvent (here water) is transferred into an ionic solution of finite concentration in the *same solvent*.

The expression of the “Born” term drew on the Born equation [Eq. (2)] but, as said above, it was not introduced by Born. Presumably, a more correct formulation would be ‘Born-like term’.

The relation was expressed by assimilating an ionic solution to a dielectric continuum of dielectric constant ϵ_{sol} , and by assuming that the Born equation could be used equally in the case of an ion in an electrolyte of finite concentration.

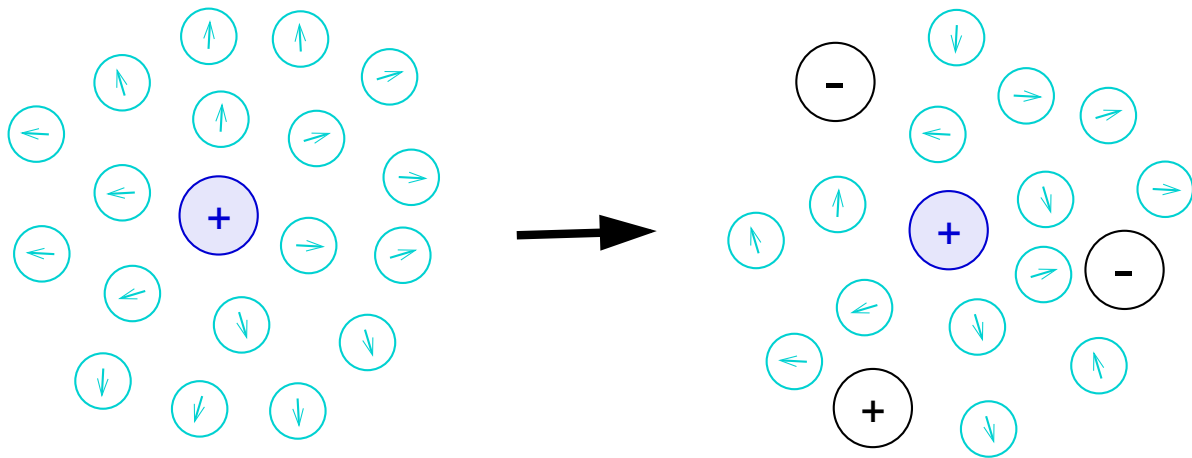


Figure 1: Illustration for the “Born” term. An ion (here a cation) is transferred from pure water (reference state) to a solution of some finite salt concentration.

Then, for the process depicted in Figure 1, in which the ion is transferred from pure solvent to a solution (the two having relative permittivities ϵ_W and ϵ_{sol} , respectively), the use of Eq. (2) leads to the formula,

$$\beta\Delta\mu_i^{(\text{“Born”})} = \frac{L_0}{\sigma_i} \left(\frac{1}{\epsilon_{sol}} - \frac{1}{\epsilon_W} \right) \quad (5)$$

where Δ denotes a difference w.r.t. infinite dilution (the reference state).

It stems from Eq. (5) that the “Born” term is always positive because the solution relative permittivity, ϵ_{sol} , is smaller than the dielectric constant of pure solvent, ϵ_W . This drop in ϵ_{sol} originates from the fact that there are fewer water molecules in a given volume of solution when the salt concentration is increased, and these water molecules become less and less effective for screening charge-charge interactions.

2.2.2. Approximate expression

It may be noticed that the “Born” term takes a still simpler form when the relative solution permittivity ϵ_{sol} has a particular dependency w.r.t. the salt concentration. Indeed, this may be seen by plotting experimental values for $1/\epsilon_{sol}$ for alkali chloride solutions at 25°C [34–36]. This plot is shown in Figure 2. It is observed that these data are very well fitted (the coefficient of determination R^2 being better than 0.98) by a function of the form: $1/\epsilon_{sol} = 1/\epsilon_W + \alpha C_s/\epsilon_W$, in which C_s is the salt concentration and $\alpha C_s/\epsilon_W$ is the slope of a fitting line in Figure 2), or equivalently,

$$\epsilon_{sol} \simeq \frac{\epsilon_W}{1 + \alpha C_s} \quad (6)$$

which was the dependency used in former work in the MSA at the McMillan-Mayer level [37, 38].

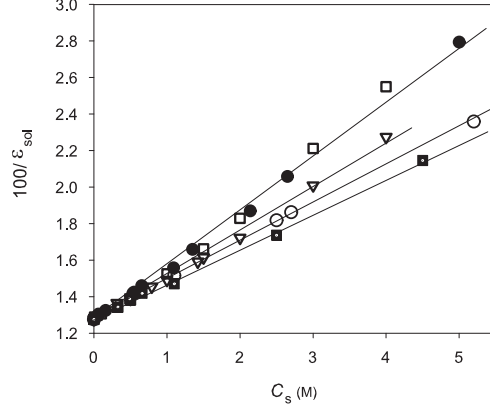


Figure 2: Experimental values of $100/\varepsilon_{sol}$ vs. salt concentration in the case of LiCl (\bullet), NaCl (\square), KCl (∇), RbCl (\circ), and CsCl (\blacksquare). Solid lines: results of linear fits (the fitting lines for LiCl and NaCl cannot be distinguished from each other).

Therefore, by using Eqs. (5) and (6), one finds that if experimental data for ε_{sol} are employed in the “Born” term, the latter reads,

$$\beta\Delta\mu_i^{(\text{“Born”})} \simeq \frac{L_W}{\sigma_i} \alpha C_s \quad (7)$$

where $L_W = L_0/\varepsilon_W$ is the Bjerrum distance, and Δ denotes difference w.r.t. infinite dilution.

Thus, if it is assumed that relation (6) holds, then the “Born” term exhibits a nearly linear variation with the concentration of the salt. A similar outcome is also observed when using the formulas proposed by Pottel [39] and Schreckenberget al. [11] as was shown in the Supplementary Material of Ref. 19.

2.2.3. A peculiarity in the expression used in the literature

Actually, Eq. (5) is not the expression usually employed in the literature. Instead, an expression for the Helmholtz energy related to the “Born” term is first written down by basically assuming that the solution permittivity is constant vs. concentration [11, 13, 17], and then this energy is differentiated to get a modified chemical potential.

This can be illustrated in the simplifying case of a uni-univalent salt for which the cation (+) and anion (-) diameters are equal: $\sigma_+ = \sigma_- = \sigma$. Hereafter, ρ_i stands for the number density of ion of type i (the number of ions per volume unit).

The Helmholtz energy is then expressed by [11, 13, 17],

$$\beta\Delta A^{(\text{“Born”}, \text{lit})}/V = \frac{L_0}{\sigma} \left(\frac{1}{\varepsilon_{sol}} - \frac{1}{\varepsilon_W} \right) \rho t \quad (8)$$

where $\rho_t = \rho_+ + \rho_-$ is the total number density of solute, and the superscript ‘lit’ denotes that this is the relation usually employed in the literature. One also arrives at this expression by integrating Eq. (5) w.r.t. the densities ρ_i by taking ε_{sol} constant.

Next, this energy is differentiated w.r.t. the number density ρ_i to obtain the chemical potential of an ion i , which yields,

$$\beta\Delta\mu_i^{(\text{“Born”}, \text{lit})} = \frac{L_0}{\sigma} \left(\frac{1}{\varepsilon_{sol}} - \frac{1}{\varepsilon_W} \right) + \frac{L_0}{\sigma} \rho_t \frac{\partial(\varepsilon_{sol}^{-1})}{\partial\rho_i} \quad (9)$$

which, as compared to Eq. (5), introduces an extra term involving a derivative of the permittivity. Thus, by virtue of the latter equation, the contribution to the mean salt chemical potential,

$$\Delta\mu_s^{(\text{“Born”}, \text{lit})} = \frac{1}{\rho_t} \sum_k \rho_k \Delta\mu_k^{(\text{“Born”}, \text{lit})} \quad (10)$$

is given by,

$$\beta\Delta\mu_s^{(\text{“Born”}, \text{lit})} = \frac{L_0}{\sigma} \left(\frac{1}{\varepsilon_{sol}} - \frac{1}{\varepsilon_W} \right) + \frac{L_0}{\sigma} \sum_k \rho_k \frac{\partial(\varepsilon_{sol}^{-1})}{\partial\rho_k} \quad (11)$$

Noting that the following relation holds,

$$\sum_k \rho_k \frac{\partial(\varepsilon_{sol}^{-1})}{\partial\rho_k} = \rho_s \frac{\partial(\varepsilon_{sol}^{-1})}{\partial\rho_s} \quad (12)$$

in which ρ_s is the number density of salt ($= \rho_+ = \rho_-$ here), and if one moreover assumes that ε_{sol}^{-1} varies linearly with concentration as in Eq. (6), then one finds that,

$$\rho_s \frac{\partial(\varepsilon_{sol}^{-1})}{\partial\rho_s} = \frac{1}{\varepsilon_{sol}} - \frac{1}{\varepsilon_W} \quad (13)$$

So, by combining the latter three relations, one finds that the second term in the r.h.s. of Eq. (11) is equal to the first one, and one obtains,

$$\Delta\mu_s^{(\text{“Born”}, \text{lit})} = 2 \Delta\mu_s^{(\text{“Born”})} \quad (14)$$

in which $\Delta\mu_s^{(\text{“Born”})}$ is the original ‘Born’ term given by Eq. (5).

This simple calculation can also be made without difficulty in the general case of ions of different sizes and arbitrary charges, and it yields the same relation as Eq. (14) when a linear variation of ε_{sol}^{-1} with the salt concentration is assumed.

The above calculation shows that the procedure used in the literature leads to an inconsistency between the original ‘Born’ term, which should be used for the chemical potential of a salt, and the modified ‘Born’ term generally utilized in the literature [a relation similar to Eq. (11)].

In the above manipulation, the original “Born” term is initially introduced in order to account for the variation of ε_{sol} with the salt concentration, C_s . But then it is integrated to get the Helmholtz energy by considering that ε_{sol} is constant vs. C_s , and finally this Helmholtz energy is differentiated w.r.t. the ion densities. In this differentiation, the dependency of ε_{sol} vs. C_s is restored, which produces an extra term.

This manipulation is inconsistent. It finally leads to a “Born” term that is the double of what it should be.

It could be proposed to lift this inconsistency by considering a particular expression for ε_{sol} as a function of C_s (such as the one of Eq. (6), or that of Pottel [39] or Schreckenberget al. [11]), and integrate Eq. (5) over number densities. However, this procedure would lead to an impasse because the “Born” term of Eq. (5) does not derive from a Helmholtz energy. Indeed, the condition: $\partial\Delta\mu_i^{(\text{“Born”})}/\partial\rho_j = \partial\Delta\mu_j^{(\text{“Born”})}/\partial\rho_i$, is not fulfilled because the following relation: $\sigma_i \partial\varepsilon_{sol}^{-1}/\partial\rho_i = \sigma_j \partial\varepsilon_{sol}^{-1}/\partial\rho_j$, cannot be expected to hold in the general case.

Therefore, the expression for the “Born” term commonly employed in the literature is not consistent with the original one. In this work, we will only consider the “Born” term of Eq. (5).

3. The “Born” term as a measure of the variation of ion-solvent interactions?

3.1. General comments

It has often been claimed that the “Born” term accounts for the change in ion-solvent interactions [4, 15–18, 40] when an ion is transferred from the reference state (infinite dilution) to a solution of some finite salt concentration. Then, in the expression of the chemical potential of an ion, this term was introduced as a supposedly natural complement to the contribution for ion-ion interactions, which is usually a Debye-Hückel (DH) or MSA term at the McMillan-Mayer level.

However, the pertinence of the “Born” term to describe the effect of ion-solvent interactions is not obvious. Indeed, even if one admits that the *static* solution permittivity ε_{sol} coincides with the experimental value, which is questionable because of several issues associated with the interpretation of experimental data [41–43] (see also Ref. 44 for an insightful review), the following fundamental question arises about Eq. (5):

Why would ε_{sol} , which reflects the strength of effective (solvent-mediated) *ion-ion forces* in a solution, be the key quantity to describe the effect of *ion-solvent interactions*? This simple question already raises questions and perplexity about the “Born” term.

Furthermore, ε_{sol} is relevant for interactions between charges separated by a large distance. This range contrasts with that of ion-solvent interactions which is typically of a few solvent molecular diameters (see also Section 3.3). Furthermore, the magnitude of ε_{sol} not only results from the effect of solvent molecules but also from that of ions (see the next section). Another feature of the “Born” term is that its magnitude is generally not small, typically of a few $k_B T$ [19], which can make it one of the dominant contributions (see Figure 4 of Ref. 13 as an example).

Therefore, this term, which has often been accepted as a matter of course in the literature, raises some basic issues. An example is presented in the next section.

3.2. A simple remark

Let us imagine a process in which an ion is transferred at constant temperature from pure water into an ionic liquid comprising this ion as depicted in Figure 3. This process may be carried out in two steps: first from pure water to a vacuum, and then from a vacuum to the ionic liquid.

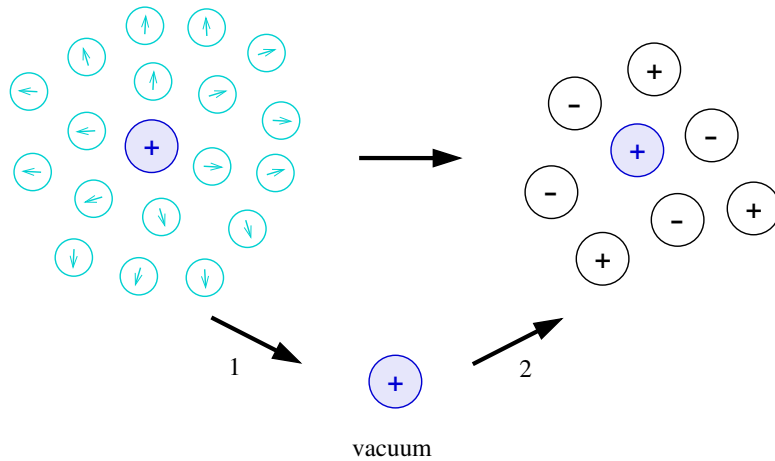


Figure 3: Transfer of a lone ion (here a cation) from pure water to an ionic liquid comprising this ion, at the same temperature.

The contribution from ion-water (iW) interactions to the chemical potential of an ion i (cation or anion) in this transfer, $\Delta\mu_i^{iW}$, can be deduced from steps 1 and 2: the first contribution is the opposite of its Gibbs hydration energy, $-\mu_i^{Hydr}$, and the second is naught since there is no water in the two states involved in step 2. Therefore, in the overall process 1+2, the change in the chemical potential corresponding to ion-water interactions is simply,

$$\Delta\mu_i^{iW} = -\mu_i^{Hydr} \quad (15)$$

Furthermore, this same quantity can be obtained from the “Born” term in which ε_{sol} is replaced with the relative permittivity of the ionic liquid (IL). By virtue of Eq. (3) (assuming

that the Born equation describes the Gibbs hydration energy of the ion, $-\mu_i^{Hydr}$), and of Eq. (5), one readily gets for the process of Figure 3,

$$\Delta\mu_i^{(\text{“Born”})} = \frac{1/\varepsilon_{IL} - 1/\varepsilon_W}{1 - 1/\varepsilon_W} \times (-\mu_i^{Hydr}) \quad (16)$$

This result is now applied to the following particular system. For a transfer below 100°C one may consider an ionic liquid like 1-butyl-3-methylimidazolium chloride (also known under the shorthand names [C4MIM][Cl] or BMIMCl), that has a melting temperature of $\sim 65^\circ\text{C}$ [45, 46]. Aqueous solutions of this salt may be prepared in a wide mole fraction range [47].

For the chloride anion, according to Eq. (15), this variation amounts to $\Delta\mu_i^{iW} = -\mu_i^{Hydr} \sim 114 k_B T$ at 65°C , if the Gibbs hydration energy is calculated using the ion-dipole MSA [19] (instead of $\sim 124 k_B T$ at 25°C [48, 49]).

On the basis of an estimation of the value of ε_{IL} for BMIMCl [50] and of the general variation of ε_{IL} with temperature for BMIM salts [51], it may be estimated that $\varepsilon_{IL} \sim 13 \pm 1$ for this salt at 65°C . The dielectric constant of water at that temperature is ~ 65 [52]. With these values one gets from Eq. (16), $\Delta\mu_i^{(\text{“Born”})} \simeq 0.06 \times (-\mu_i^{Hydr})$ (corresponding to a value of $\sim 7 k_B T$), instead of $-\mu_i^{Hydr}$ as prescribed by Eq. (15). So, in this example, the result from the “Born” term is ~ 16 times smaller than the actual variation of the ion-water contribution to the chemical potential of a cation or anion in the transfer of Figure 3.

This discrepancy originates from the presence of the term $1/\varepsilon_{IL}$ in the numerator of Eq. (16) for the “Born” term. If this term was equal to 1, then one would recover the correct result, $-\mu_i^{Hydr}$. But the IL itself has a dielectric constant that is significantly larger than 1, and this is why the correct result is not obtained. The relatively high value of the permittivity of the BMIMCl ionic liquid stems in particular from the strong permanent dipole moment of the BMIM⁺ cation [53] and from the polarizability of the ions.

This example highlights the fact that the mismatch is due to the effect of the ions in the final state of Figure 3. The “Born” term involves the permittivity of the system, which includes the effect of the solvent, and also *of the ions*. This shortcoming is illustrated in the extreme case considered here of a transfer into an IL, but it would be also at play at any concentration of the salt in the solution.

This simple model-independent example shows that the “Born” term is an improper way of estimating the effect of ion-solvent interactions.

3.3. A Born-type formula as an alternative to the “Born” term?

The subject of this section was motivated by the observation that, to the best knowledge of this author, a calculation of the solvation energy of an ion in a solution has never been presented,

in which a method similar to that utilized by Born to derive his famous equation [2] would be employed. This is done in this section in the case of a dilute ionic solution.

As in the derivation of the Born equation, the solvent is viewed as a dielectric continuum, and the purpose is to calculate the energy of the electric field created by a central ion C in the solvent. As compared to the situation approached by Born, ion C is not alone in the dielectric, it is now surrounded by positive and negative ions.

The main expected effect of the salt ions is that the latter will partially screen out the electric field created by the central ion, which will reduce the magnitude of the field in the solvent around C. It is therefore expected that the interaction energy of C with the solvent would be *lower* than in the case where C is alone in the solvent (case of the Born equation, Eq. (5)). Accordingly, the corresponding Born-like term (without quotes) would be negative, a behavior that would be opposite to the “Born” term.

The details of the calculation are presented in the Supplementary Material. The final result for the variation of the solvation energy of the central ion w.r.t. infinite dilution, ΔW_i , at very low salt concentration is,

$$\beta\Delta W_i \simeq -\frac{3}{4} L_W \kappa \quad (17)$$

so that ΔW_i is indeed negative as expected.

However, Eq. (17) shows that $\beta\Delta W_i$ varies as the square root of the salt concentration because $\kappa = (8\pi L_W \rho_s)^{1/2}$ for this 1:1 salt. This is an unwelcome result because it has the same κ -dependence as the DH limiting law (DHLL) which reads,

$$\beta\mu_i^{DHLL} = -\frac{1}{2} L_W \kappa \quad (18)$$

Therefore, in a model with explicit solvent in which the ion-ion and ion-solvent contributions would be added up, combining Eqs. (17) and (18) would result in a violation of DHLL, because ΔW_i also varies as $\sqrt{C_s}$.

Incidentally, it is noticed that this is not the case of the “Born” term if, as is observed for the experimental solution permittivity, the variation of $1/\varepsilon_{sol}$ is proportional to C_s ($\varepsilon_{sol}^{-1} - \varepsilon_W^{-1} \propto C_s$). In the same way, the MSA-ID permittivity, and its inverse, vary as C_s at low concentration [see Eq. (A.1)], so that the DHLL is indeed fulfilled.

Therefore, Eq. (17) is an unphysical result for this problem. Nevertheless, it might be expected that the ionic cloud around C indeed produces a screening of the electric field in the dielectric, and an ensuing reduction of W_i . We note that no mention of this effect is present in the “Born” term. But something is clearly missing in the present calculation. The present

procedure only involves a calculation of the electrostatic energy in the dielectric, it does not account for entropic effects for the solvent particles. But this was also the principle of the calculation that was made by Born to establish his equation, of which Born himself seemed to be quite ‘skeptical’... [24] (it is clear however that an entropic contribution is obtained by differentiation of the Helmholtz energy found by Born w.r.t. temperature T , because the permittivity of solution varies with T). So the present simple model apparently leads to some tricky questions that will require further analysis. In the absence of a clear answer, this problem will be reserved for future investigation.

4. Examination of the problem in the case of a mixture of ions and dipoles

In this section, some previous results [19] are recalled and expressed in a more explicit and significant way. It is instructive to study the present problem in the simple case of a binary mixture of hard spherical ions and dipoles, the latter mimicking water molecules. It is assumed that the cation and the anion of the salt have the same diameter and opposite charges, and that the solvent particles bear a central point dipole but are not polarizable. Then, the two types of ions have the same chemical potential.

For this model system, the interactions between the particles are pairwise additive (unlike, e.g., forces induced by polarization). The electrostatic part of the chemical potential of an ion i (cation or anion) splits into ion-ion (ii) and ion-dipole (id) contributions as,

$$\beta\mu_i^{el} = \beta\mu_i^{ii} + \beta\mu_i^{id} \quad (19)$$

In this relation, the chemical potentials μ_i^{ii} and μ_i^{id} are for direct interparticle forces in a vacuum. The ion-ion contribution μ_i^{ii} contains an influence of the solvent dipole moment, and μ_i^{id} vanishes when the dipole moment is zero.

The Gibbs solvation energy of ion i , μ_i^{Hydr} , may be subtracted from each side of Eq. (19), which yields,

$$\beta\Delta\mu_i^{el} = \beta\mu_i^{ii} + \beta\Delta\mu_i^{id} \quad (20)$$

because, at infinite dilution of the ions, μ_i^{ii} goes to zero so that no “ Δ ” needs be added to it, and $\mu_i^{id} \rightarrow \mu_i^{Hydr}$.

At low salt concentration, it may be conjectured that

$$\beta\mu_i^{ii} \simeq -L_0\kappa/2 \quad (21)$$

which is the DH limiting law for direct ion-ion interactions (in a vacuum), as was found within the MSA-ID [19].

Therefore, Eq. (20) may be rewritten as,

$$\beta\Delta\mu_i^{el} = \beta\mu_i^{ii} \frac{1}{\varepsilon_W} + \left[\beta\Delta\mu_i^{id} + \beta\mu_i^{ii} \left(1 - \frac{1}{\varepsilon_W} \right) \right] \quad (22)$$

in which, by virtue of Eq. (21), the first term on the r.h.s. is the DH limiting law (DHLL), Eq. (18), in a model with *implicit* solvent of dielectric constant ε_W [19],

$$\beta\mu_i^{ii} \frac{1}{\varepsilon_W} \simeq \ln \gamma_i^{DHLL} \quad \text{when } C_s \rightarrow 0 \quad (23)$$

where γ_i denotes the activity coefficient of ion i and $\ln \gamma_i^{DHLL} = -L_W \kappa/2$ [Eq. (18)].

It is useful to separate this DHLL term in Eq. (22) because, at low salt concentration, it is involved in all explicit-solvent models in which an ion-ion contribution for implicit solvent (DH or MSA, the latter being equivalent to the former at high dilution) is used, as is generally done, e.g., in SAFT-type models [10–13].

Then, again at low salt concentration, one gets from Eqs. (22) and (23),

$$\beta\Delta\mu_i^{el} = \ln \gamma_i^{DHLL} + \beta\Delta\mu_i^{id(resc)} \quad (24)$$

where

$$\beta\Delta\mu_i^{id(resc)} = \beta\Delta\mu_i^{id} + \beta\mu_i^{ii} \left(1 - \frac{1}{\varepsilon_W} \right) \quad (25)$$

is a rescaled ion-dipole chemical potential [19].

These latter two relations pinpoint the contribution that is needed (at high dilution) in explicit-solvent electrolyte models for a combination with an implicit-solvent term for ion-ion interactions.

Eq. (25) shows that it should include the contribution from direct ion-dipole interactions, and the most part of the direct ion-ion interactions (second term of the r.h.s. of Eq. (25)). The latter corresponds to the ion-ion interactions that do not contribute to the reaction field (which reduces the magnitude of the electric field acting on ion i , by a factor of ε_W at large dilution).

In Eq. (25), one has $\Delta\mu_i^{id} > 0$ (and $\mu_i^{id} < 0$) but it decreases in absolute value when the salt concentration is increased, and $\mu_i^{ii} < 0$. So, the ion-ion part gives a negative contribution that lowers (significantly [19]) the direct ion-dipole part. The result, $\Delta\mu_i^{id(resc)}$, can be positive as $\Delta\mu_i^{id}$, or negative if the ion-ion contribution is sufficiently large. There is a priori no restriction on the sign of $\Delta\mu_i^{id(resc)}$.

5. Expressions for mixtures of ions and dipoles within the MSA-ID

The MSA for ion-dipole mixtures (MSA-ID) is a model with explicit solvent for ionic solutions, in which the solvent molecule is represented by a sphere bearing a point dipole at its

center and ions are charged hard spheres as depicted in Figure 1. The MSA-ID has been solved in the case of equisized ions [21, 54], and in the general case of ions and dipoles of arbitrary sizes [23, 55, 56].

This model lacks features like the presence of hydrogen bonds, but it is the only analytical model with a firm statistical-mechanical basis in which all interactions between species are treated consistently at the same level. A silver lining of the MSA-ID is that it makes it possible to obtain ion-ion and ion-solvent contributions to ion chemical potential, which includes entropic effects. As such, and despite it is an approximate treatment, it can provide a useful framework and reference system to try to better understand the properties of real ionic solutions.

5.1. Case of a dilute electrolyte in a waterlike solvent within the MSA-ID

In this section, some results obtained using the MSA-ID model [19] are recalled in a slightly different manner and some new results are presented for ions of different diameters. Moreover, the “Born” term is calculated within the MSA-ID with the formula usually employed in the literature for this term. In what follows, the contributions will be computed at constant solvent concentration (constant ρ_W).

In previous work [19], the “Born” term was first investigated using the semi-restricted MSA-ID in which both ions have the same size [21, 54], in a waterlike solvent made up of molecules of arbitrary size. The diameter and dipole moment of the solvent molecule were determined, which allowed one to recover the density and the dielectric constant of water at 1 atm and 25°C, which gave: $\sigma_W \simeq 2.4805 \text{ \AA}$, and $m_W \simeq 2.2203 \text{ D}$. The effective solution permittivity, ε_A , may be calculated within the MSA-ID framework [19, 21] by following the method proposed by Adelman [57].

The basic equations used in the semi-restricted MSA-ID (for which $\sigma_+ = \sigma_- = \sigma_i$) are recalled in the Supplementary Material. They were solved using the symbolic computation program Maple.

It was shown in Ref. 19 that at low salt concentration and for constant solvent concentration, the variation of the chemical potential of either ion (cation or anion) for this model system is given by,

$$\beta \Delta \mu_i^{id(resc)} \sim \frac{L_0}{\sigma_i} M d_0^2 \quad (26)$$

in which the formula for M is provided in Appendix A together with the expansion of ε_A at low concentration (not formulated in Ref. 19), and,

$$d_0^2 = 8\pi L_0 \sigma_i^2 \rho_s \quad (27)$$

where d_0 is a dimensionless parameter for the ions, and the expression of M is given in Eq. (A.4) in terms of a MSA-ID parameter λ that has a value of ~ 2.6535 at 25°C for a waterlike solvent, and of the size ratio $r = \sigma_W/\sigma_i$. The parameter λ is related to the energy of dipole-dipole interactions in pure solvent (through the parameter b_2 [21]), and to ε_W through the relation,

$$\varepsilon_W = [\lambda(\lambda + 1)^2/4]^2 \quad (28)$$

It is seen in Eq. (26) that $\Delta\mu_i^{id(resc)}$ is proportional to C_s (by virtue of Eq. (27)), which contrasts with the expression for $\Delta\mu_i^{id}$ which was shown to vary with $\sqrt{C_s}$ [19].

The Debye screening parameter at large dilution is given by,

$$\kappa^2 = 8\pi L_0 \rho_s / \varepsilon_W, \quad (29)$$

which entails together with Eq. (27) that,

$$d_0 = \kappa \sigma_i \sqrt{\varepsilon_W} \quad (30)$$

So, d_0 is proportional to the Debye parameter κ .

At 25°C one obtains by using $\sigma_W \simeq 2.4805 \text{ \AA}$ and $\lambda \simeq 2.6535$ [19],

$$\beta\Delta\mu_i^{id(resc)} \simeq 15.885 \frac{(\sigma_i + 4.6138)(\sigma_i - 3.5364)}{(\sigma_i + 0.93482)^4} C_s \quad (31)$$

with the diameter σ_i and the salt concentration C_s expressed in \AA and mol L^{-1} , respectively.

In the same way, an expression for the ‘‘Born’’ term can be obtained from Eq. (5) in which ε_{sol} is replaced with ε_A calculated within the MSA-ID. Note that a slightly different expression for the ‘‘Born’’ term was taken in Ref. 19; the one used here is identical to the relation commonly used in the literature for this term [11, 17]. One gets,

$$\beta\Delta\mu_i^{(‘‘Born’’)} = \frac{L_0}{\sigma_i} B_0 d_0^2 \quad (32)$$

where the expression for B_0 is given in Appendix A. At 25°C , one finds from Eq. (32) (with σ_i in \AA),

$$\beta\Delta\mu_i^{(‘‘Born’’)} \simeq 21.137 \frac{(\sigma_i + 0.63714)}{\sigma_i(\sigma_i + 0.93482)^2} C_s \quad (33)$$

Eqs. (31) and (33) give the initial behavior of $\beta\Delta\mu_i^{id(resc)}$ and $\beta\Delta\mu_i^{‘‘Born’’}$ as a function of C_s in the semi-restricted MSA-ID. Both exhibit a linear variation with C_s at very low concentration. Thus, the two vary as κ^2 , unlike the DH ion-ion contribution which scales as κ .

The particular case of RbCl is considered now because the Shannon and Prewitt diameters [58–60] of Rb^+ and Cl^- are very close to each other ($\sigma_{\text{Rb}^+} \sim 3.32 \text{ \AA}$, $\sigma_{\text{Cl}^-} \sim 3.34 \text{ \AA}$) so that the semi-restricted MSA-ID may be employed.

The classic “Born” term, $\beta\Delta\mu_i^{(\text{“Born”})}$ [Eq. (33)], and the rescaled, $\beta\Delta\mu_i^{id(resc)}$ [Eq. (31)], computed within the MSA-ID, are plotted in Figure 4 up to a concentration of 0.01 M. In this concentration range, $\beta\Delta\mu_i^{id(resc)}$ and $\beta\Delta\mu_i^{(\text{“Born”})}$ are nearly linear vs. C_s .

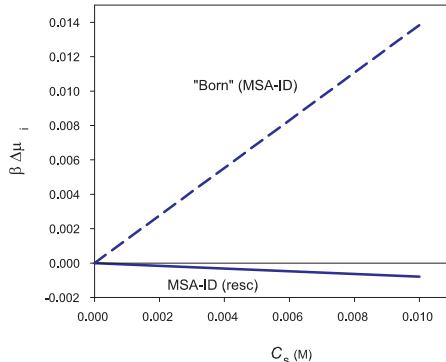


Figure 4: Plot of $\beta\Delta\mu_i^{id(resc)}$ [Eq. (31)] (solid line) and of the “Born” term $\beta\Delta\mu_i^{(\text{“Born”})}$ [Eq. (5)] (dashed line), both computed within the MSA-ID, in the case of RbCl solution at low concentration.

It is seen in this figure that the rescaled ion-dipole contribution is much lower, and of opposite sign, as compared to the “Born” term when both are computed within the MSA-ID model.

Next, the initial slopes of the rescaled and “Born” terms (at high dilution of the salt), $\beta\Delta\mu_i^{id(resc)}/C_s$ and $\beta\Delta\mu_i^{(\text{“Born”})}/C_s$, were investigated using the general *unrestricted* MSA-ID model in which the ion sizes can have different values. The solution to the unrestricted MSA-ID model was given recently [23]. Here, it makes it possible to consider the case of aqueous alkali chloride solutions: LiCl, NaCl, KCl, and RbCl. At very low concentration, the electrostatic contribution to the chemical potential of an ion is very well approximated by the internal energy per particle, u_i , which makes the calculation easier. The formulas being quite involved though, it is not possible to reproduce them here.

These initial slopes are plotted in Figure 5. The diameters of the ions were taken from Shannon and Prewitt tables [58–60] (for a coordination number of 6; $\sigma_{Li^+} = 1.80 \text{ \AA}$ to $\sigma_{Rb^+} = 3.32 \text{ \AA}$). The values of the initial slope $\beta\Delta\mu_i^{(\text{“Born”})}/C_s$ were obtained by replacing ε_{sol} in Eq. (5) with its MSA-ID counterpart (ε_A) [19]. The curves for cation and anion merge on the r.h.s. of Figure 5 when arriving at RbCl because the diameters of the Rb^+ and Cl^- ions are nearly equal.

Figure 5 shows that, at high dilution, the rescaled ion-dipole contribution, $\beta\Delta\mu_i^{id(resc)}$, is negative for alkali cations and the chloride anion. This behavior contrasts with that of the “Born” term which is always positive. The latter is nearly constant in the case of the chloride

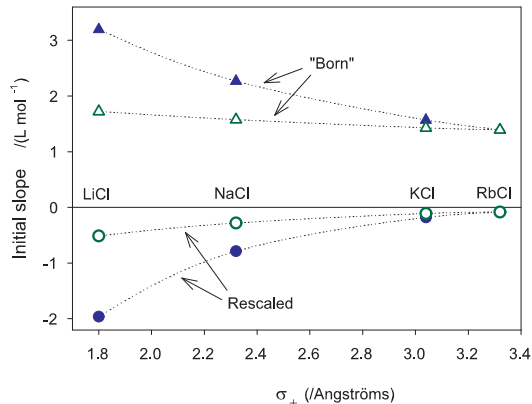


Figure 5: Initial slopes of rescaled and “Born” contributions, $\beta\Delta\mu_i^{id(resc)}/C_s$ and $\beta\Delta\mu_i^{“Born”}/C_s$, respectively, computed within MSA-ID, for various alkali ions (full symbols) and chloride ion (empty symbols) in alkali chloride salt solutions. Triangles: “Born” term; Circles: rescaled term. The plots are drawn against the Shannon and Prewitt cation diameter, σ_+ .

anion and significantly larger than the rescaled term. The “Born” term is of the same order of magnitude (in absolute value) as the rescaled term in the case of the Li^+ cation, and it becomes progressively relatively larger as one moves to bigger cations.

The outcome that the rescaled ion-dipole contribution, $\Delta\mu_i^{id(resc)}$, can be negative must not come as a surprise. It results from the fact that the “Born” term is generally used in conjunction with an ion-ion term for *implicit* solvent, as expressed in Eq. (24). Then, as seen in Eq. (25) and discussed below this equation, the rescaled $\Delta\mu_i^{id(resc)}$ being the sum of two quantities of opposite signs, it can be positive or negative. This outcome is related to the fact that $\Delta\mu_i^{id(resc)}$ has no simple physical meaning. In contrast, the original, non-rescaled, $\Delta\mu_i^{id}$ for direct interactions is always positive for any salt concentration.

5.2. Limit of low density and high temperature within the MSA-ID

In this section, the semi-restricted MSA-ID is employed in the case of a very weakly coupled ion-dipole mixture at low ion and dipole density. Weak coupling means that the mixture is studied at high temperature, or equivalently for low ion charge and solvent dipole moment.

It is shown in Appendix B that the MSA becomes exact in the low-density and high-temperature limit. This property is used below for a test of the “Born” term against the rescaled ion-dipole result. In this comparison, both terms are calculated within the MSA-ID framework, by using the expressions for B_0 and M [Eqs. (A.3) and (A.4)].

So, in this section, the system is very dilute, it is a plasma made up of ions and dipoles. The interaction potentials are much weaker than the mean thermal agitation energy, that is

$\beta V_{ij}(r) \ll 1$ for all r outside the hard cores ($\beta = 1/k_B T$). This is equivalent to saying that the dimensionless coupling parameters,

$$q^{*2} = \frac{\beta e^2}{4\pi\epsilon_0\sigma_i} = \frac{L_0}{\sigma_i}, \quad m^{*2} = \frac{\beta m_W^2}{4\pi\epsilon_0\sigma_W^3} \quad (34)$$

are very small compared to unity: $q^{*2} \ll 1$ and $m^{*2} \ll 1$. In the definition of m^* , m_W is the solvent dipole moment.

In Eq. (34), q^{*2} and m^{*2} are the electrostatic to mean thermal energy ratios for ion-ion and dipole-dipole interactions at contact, respectively. Other dimensionless parameters involved in the MSA-ID are d_0 for the ions, defined in Eq. (27), and d_2 which is given by,

$$d_2^2 = \frac{\beta m_W^2}{3\epsilon_0} \rho_W \quad (35)$$

for the dipolar solvent.

One has from Eqs. (27), (34), and (35),

$$d_0^2 = 8\pi\sigma_i^3 q^{*2} \rho_s, \quad d_2^2 = \frac{4}{3}\pi\sigma_W^3 m^{*2} \rho_W \quad (36)$$

Hence, d_0^2 and d_2^2 are proportional to the densities of salt and dipoles, ρ_s and ρ_W , respectively.

Now, if it is assumed that the ions and the dipoles are very dilute, then one also has: $d_0^2 \ll 1$ and $d_2^2 \ll 1$. Since the dipoles are very dilute, the value of the parameter λ is close to 1 ($\lambda > 1$), which is its value for a vacuum [19, 21]. In that case, one has using Eq. (28),

$$\epsilon_W \simeq 1 + 4(\lambda - 1) \quad (37)$$

to first order in $(\lambda - 1)$.

Then, Eqs. (A.3) and (A.4) for B_0 and M , that were established for low salt concentration (and constant dipole density), may now be expanded in Taylor series in the vicinity of $\lambda = 1$.

One obtains,

$$\beta\Delta\mu_i^{id(resc)} = -\frac{2}{3}\frac{r^3}{(r+1)^2}(\lambda-1)d_0^2 \quad (38)$$

and,

$$\beta\Delta\mu_i^{("Born")} = \frac{4}{9}\frac{r^3}{(r+1)^2}(5r+8)(\lambda-1)^2 d_0^2 \quad (39)$$

in which $r = \sigma_W/\sigma_i$ is the same for the two ions (because $\sigma_+ = \sigma_-$).

The ratio of the two is,

$$\frac{\beta\Delta\mu_i^{("Born")}}{\beta\Delta\mu_i^{id(resc)}} = -\frac{2}{3}(5r+8)(\lambda-1) \quad (40)$$

Eqs. (38)-(40) are expected to be exact results in the limit of low density and low coupling (high temperature, or low charge and low dipole moment).

The rescaled and “Born” terms in Eqs. (38) and (39) scale as d_0^2 , which is proportional to C_s . On the other hand, the rescaled $\beta\Delta\mu_i^{id(resc)}$ is negative whatever the relative sizes of the ions and dipoles, and it scales as $(\lambda - 1)$, which contrasts to the “Born” term which is always positive and scales as $(\lambda - 1)^2$.

So, for the present system, the “Born” term is in sharp contrast to the correct rescaled ion-dipole contribution.

6. Conclusion

The “Born” term is based on an improper extrapolation of the Born equation [Eq. (2) or (3)] to the case of solutions of finite salt concentration. It is an empirical formula to which the name of Born has been unduly (and unfairly) tied. Moreover, an inconsistent formula has been commonly used in the literature.

It has often been claimed to represent the effect of ion-solvent interactions in models with explicit solvent. In keeping with former work [19], this study arrives at a negative conclusion on this point. For every single situation considered here, it has been found that the “Born” term provides an unsuitable or inaccurate description for that purpose.

General considerations about a system of ions and dipoles suggest the introduction of a ‘rescaled’ ion-solvent term for a suitable match with the term adopted for ion-ion interactions, which is commonly a DH or MSA term, the latter being usually employed in implicit-solvent models for electrolytes. This modified ion-solvent term combines contributions from direct ion-solvent and ion-ion interactions, which does not lend a simple physical meaning to this term. It can be positive or negative, which is in contrast to the “Born” term which is always positive.

However, no suitable term is really available yet to replace the “Born” term. The calculation of a Born-like term as proposed in Section 3.3 yields an unphysical result, in violation of the DHLL at low salt concentration. Nonetheless, maybe this derivation could be amended and provide a better expression. This possibility will be examined in the future.

It could be proposed to employ the MSA-ID model for the full electrostatic contribution in explicit-solvent models, as has been done in a few works, in particular in a few SAFT models [61–63]. Promising results were obtained in Ref. 63 within the semi-restricted MSA-ID. In this respect, it may be noted that the solution to the general unrestricted case, possibly including the effect of solvent polarization, is now available [23, 64]. However, it must be recognized that

the MSA-ID is an approximate theory, and modeling the water molecule as a dipole might be insufficient [65, 66], but maybe more progress could be made within this framework.

Meanwhile, something has to be done because the “Born” term can be a major drag for the development of reliable explicit-solvent models for electrolytes. As suggested previously, a first temporary remedy could be to introduce a multiplicative adjustable parameter to the “Born” term, that could take positive or negative values [19]. This simple modification would provide some flexibility to the “Born” term, whose magnitude is imposed in the models in which it is used. It could bring up some improvement until a better solution is found.

It is also hoped that more simulations (e.g., of the type developed in Ref. 20, combining Monte-Carlo and molecular dynamics algorithms) will be carried out in the future about this topic. They could provide some more fundamental information about the “Born” term, and some clues for its replacement.

In future work, the case of models with implicit solvent [15, 40, 67] will be considered. The relevance of the “Born” term in such models will be investigated. It must be noted that an implicit solvent model is naturally developed at the McMillan-Mayer level, at which ion-solvent interactions should not be considered explicitly. Only effective solvent-averaged ion-ion forces in the infinite dilute solution are normally involved in the MM framework [68]. This point will require further study. The relevance of a “Born” term in this type of model will be examined in the near future.

Supplementary Material

The Supplementary Material contains a demonstration of Eq. (17) for the solvation energy of an ion in a dilute electrolyte calculated in the spirit of Born, and a summary of the equations used for the semi-restricted MSA-ID in Section 5.1.

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Appendix A. Expansion of ε_A , and formulas for B_0 in Eq. (32) and M in Eq. (26)

The expansion of ε_A at low salt concentration (low d_0) is given by the following formula,

$$\varepsilon_A \simeq \varepsilon_W - E d_0^2 \tag{A.1}$$

with,

$$E = \frac{1}{128} r^3 (\lambda - 1)^2 \frac{(\lambda^2 + 3\lambda + 4)^2 (\lambda^3 + 2\lambda^2 + \lambda + 4)^2 (4\lambda^2 + 3r\lambda + 4\lambda + 2r)(\lambda + 3)}{\lambda^2 (\lambda + 2) (\lambda + r)^2 f} \quad (\text{A.2})$$

where $r = \sigma_W / \sigma_i$, and

$$f = \lambda^7 + 6\lambda^6 + 15\lambda^5 + 20\lambda^4 + 15\lambda^3 + 6\lambda^2 + 9\lambda + 24$$

from which one gets using Eqs. (5) and (32),

$$B_0 = E / \varepsilon_W^2 \quad (\text{A.3})$$

with

$$\varepsilon_W = \frac{\lambda^2 (\lambda + 1)^4}{16}$$

Moreover, one has,

$$M = -\frac{1}{16} r^3 (\lambda - 1) (\lambda^2 + 3\lambda + 4) (\lambda^3 + 2\lambda^2 + \lambda + 4) (M_2 r^2 + M_1 r + M_0) / [\lambda^5 (\lambda + 1)^8 (\lambda + 2) (\lambda + r)^4 f] \quad (\text{A.4})$$

where

$$M_2 = (\lambda + 1) (\lambda^{13} + 12\lambda^{12} + 64\lambda^{11} + 200\lambda^{10} + 406\lambda^9 + 560\lambda^8 + 452\lambda^7 - 40\lambda^6 - 399\lambda^5 - 28\lambda^4 + 436\lambda^3 + 320\lambda^2 + 1088\lambda + 3072)$$

$$M_1 = -64\lambda (3\lambda^8 + 19\lambda^7 + 44\lambda^6 + 42\lambda^5 + 3\lambda^4 - 25\lambda^3 - 66\lambda^2 - 212\lambda - 192)$$

$$M_0 = -128\lambda^2 (\lambda^8 + 7\lambda^7 + 19\lambda^6 + 25\lambda^5 + 15\lambda^4 + \lambda^3 - 19\lambda^2 - 73\lambda - 72)$$

Appendix B. Limit of low density and high temperature

A general closure relation in the field of integral equation theory is [69],

$$c_{ij}(r) = -\beta V_{ij}(r) + h_{ij}(r) - \ln g_{ij}(r) + B_{ij}(r) \quad (\text{B.1})$$

where c_{ij} , h_{ij} ($= g_{ij} - 1$), B_{ij} , and V_{ij} are the direct correlation function, the total correlation function (g_{ij} being the $i-j$ radial distribution function), the bridge function, and the interaction potential between particles i and j at distance r , respectively.

An interesting point about the bridge function $B_{ij}(r)$ is that it is of second order in density in dilute systems [69], so that it may be neglected as compared to the other terms of Eq. (B.1) in that case. This approximation leads to the hypernetted chain (HNC) closure equation,

$$c_{ij}(r) \simeq -\beta V_{ij}(r) + h_{ij}(r) - \ln g_{ij}(r) \quad (\text{B.2})$$

For a system that is dilute in all components, one also has [70],

$$g_{ij}(r) \simeq \exp[-\beta V_{ij}(r)] \quad (\text{B.3})$$

for $r > \sigma_{ij}$, where $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ is the minimum distance of approach for particles i and j .

Now, it is assumed that the temperature of the system is very high so that $\beta V_{ij}(r) \rightarrow 0$ outside the hard cores (or equivalently, $m^{*2} \rightarrow 0$ and $q^{*2} \rightarrow 0$). Then, in that limit of very low coupling, and by virtue of Eq. (B.3), Eq. (B.2) becomes,

$$c_{ij}(r) \simeq -\beta V_{ij}(r) + \mathcal{O}([\beta V_{ij}(r)]^2) \quad (\text{B.4})$$

in which the last term means a contribution of at least second order in $\beta V_{ij}(r)$.

Consequently, one obtains from this latter relation that c_{ij} is given by the MSA: $c_{ij}(r) \simeq -\beta V_{ij}(r)$, in the limit of low density and high temperature (low coupling). Then, results from the MSA become asymptotically exact in these limits.

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Supplementary Material to the paper entitled ‘Further reflections about the “Born” term used in thermodynamic models for electrolytes’

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1. Born-type formula for an ion in a dilute electrolyte

This section presents the calculation yielding Eq. (17) of Section 3.3.

As in the Born treatment for the calculation of the solvation energy of an ion [1], the energy of the electrostatic field in a small volume $d\tau$ of the dielectric is given by $dW_i = 1/2 \mathbf{D} \cdot \mathbf{E} d\tau = 1/2 \varepsilon_0 \varepsilon_r E^2 d\tau$, in which \mathbf{D} ($= \varepsilon_0 \varepsilon_r \mathbf{E}$) and \mathbf{E} are the displacement vector and the electric field in the volume $d\tau$, respectively. The situation is depicted in Figure S1. It is considered that a positive ion is located at a fixed central position. This central cation is designated by C.

For simplicity, the added salt is comprised of monovalent hard spherical cations and anions of the same diameter σ_i .

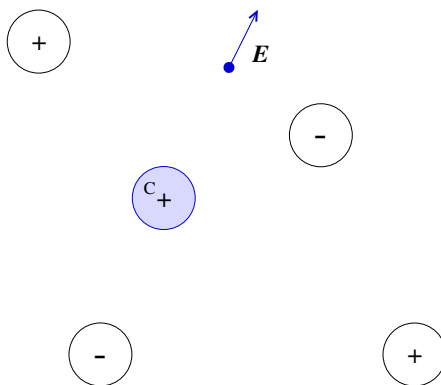


Figure S1: Illustration of the situation considered in section 3.3. C is a fixed central cation. In the calculation, the concentration of the salt is supposed to be very small.

As compared to the situation in which Born calculated the solvation energy (a lone ion in a dielectric), ion C is now surrounded by positive and negative ions (at a very low concentration in this case). Thus, a small portion of space is occupied by salt ions, and so there are fewer solvent molecules interacting with C. The main effect of the salt ions is that they screen out partially the electric field created by C, which reduces the magnitude of the field in the solvent around C. As a consequence, it may be expected that the interaction energy of C with the solvent will be lower than in the case where C is alone in the solvent.

Since the electrolyte is very dilute, the Debye-Hückel theory may be employed to address this problem. In this framework, the linearized Poisson-Boltzmann equation reads [2],

$$\Delta\psi(r) = 2\rho_s \frac{\beta e^2}{\varepsilon_0 \varepsilon_r} \psi(r) \quad (\text{S1})$$

where Δ is the Laplace operator, $\psi(r)$ is the potential of the self-consistent electrostatic field $E(r)$ at a distance r from the central ion, ρ_s is the number density of the salt (number of salt ‘molecules’ dissolved in the solvent), and ε_r is the relative permittivity of the solvent at a distance r from C.

If this relative permittivity is considered to deviate from the dielectric constant ε_W because of the presence of the ions, then the quantity ρ_s/ε_r which appears in Eq. (S1) may be approximated by ρ_s/ε_W to the first order in ρ_s when ρ_s is very small. Hence, the classic DH formula for the electrostatic potential ψ at a distance r from the central ion may be employed [2], that is,

$$\psi(r) = \frac{e}{4\pi\varepsilon_0\varepsilon_W} \frac{1}{1 + \kappa\sigma_i} \frac{\exp[-\kappa(r - \sigma_i)]}{r} \quad (\text{S2})$$

where κ is the Debye screening parameter defined by,

$$\kappa^2 = 8\pi L_W \rho_s, \quad \text{with} \quad L_W = \beta e^2 / (4\pi\varepsilon_0\varepsilon_W) \quad (\text{S3})$$

in which L_W is the Bjerrum length in water. In the case of water at 25°C, $L_W \sim 7.15$ Å.

By differentiation of ψ w.r.t. r [Eq. (S2)] one obtains the electric field $E = -d\psi/dr$,

$$E = \frac{e}{4\pi\varepsilon_0\varepsilon_W} \frac{1 + \kappa r}{1 + \kappa\sigma_i} \frac{\exp[-\kappa(r - \sigma_i)]}{r^2} \quad (\text{S4})$$

This field results from the effect of the central ion and of the ions in the ionic cloud.

Then, following the calculation of Born [1], the energy of the field E in the dielectric in the presence of salt is,

$$W_i^{(s)} = \frac{1}{2} \varepsilon_0 \varepsilon_W \int_{\sigma_i/2}^{\infty} E^2 d\tau \quad (\text{S5})$$

where $d\tau = 4\pi r^2 dr$, the integration is performed from the surface of the central ion at $r = \sigma_i/2$, and it is assumed that ε_r may be replaced with ε_W . Since the solution is very dilute, it is assumed that E is given by its expression in free space for $\sigma_i/2 < r < \sigma_i$, that is $E = e/(4\pi\varepsilon_0\varepsilon_W r^2)$. For $r > \sigma_i$, Eq. (S4) is used in Eq. (S5).

It is noted that the fraction of space occupied by the ions is not in Eq. (S5) because it is proportional to ρ_s which is of order κ^2 . It may be neglected because, as seen below, the variation of W_i is of order κ as expected from the effect of screening.

After some simple algebra one gets,

$$\beta W_i^{(s)} = \beta W_i \left[\frac{1}{2} + \frac{1}{2} \frac{1 + \kappa\sigma_i/2}{(1 + \kappa\sigma_i)^2} \right] \quad (\text{S6})$$

with W_i the electrostatic energy of the lone ion i in the dielectric [1] [Eq. (2)].

Then, it stems from the latter relation that the variation of the solvation energy of the central ion, $\Delta W_i = W_i^{(s)} - W_i$, to the leading order in κ is, $\beta\Delta W_i \simeq -3/4 \kappa\sigma_i \times (\beta W_i)$, and since by virtue of Eq. (2) one has $\beta W_i = L_W/\sigma_i$ with $L_W = L_0/\varepsilon_W$, one finally obtains,

$$\beta\Delta W_i \simeq -\frac{3}{4} \kappa L_W \quad (\text{S7})$$

2. Equations for semi-restricted MSA-ID

The semi-restricted case model involves the following two adimensional parameters,

$$d_0^2 \equiv 8\pi \rho_s L_0 \sigma_i^2, \quad (\text{S8})$$

for the ions, and

$$d_2^2 \equiv \beta \frac{\rho_W m_W^2}{3}. \quad (\text{S9})$$

for the dipolar solvent.

Moreover, 3 parameters, denoted as b_0 , b_1 and b_2 , are involved in the equations. They are functions of the ion-ion, ion-dipole, and dipole-dipole correlation functions (see Eqs. (11)-(13) of Ref. 3), respectively.

For a given ion-dipole mixture, these 3 parameters are the unknowns to be determined first in order to compute the thermodynamic quantities. The 3 basic equations of the model to be solved in the first place are [3],

$$a_1^2 + a_2^2 = d_0^2, \quad (\text{S10})$$

$$a_1 K_{10} - a_2(1 - K_{11}) = d_0 d_2, \quad (\text{S11})$$

$$K_{10}^2 + (1 - K_{11})^2 = y_1^2 + d_2^2, \quad (\text{S12})$$

where

$$a_1 = \frac{1}{2D_F^2} (\Delta - 2\beta_6 D_F), \quad a_2 = -\frac{b_1}{2\beta_6 D_F^2} \left(\frac{\Delta}{2} + \frac{D_F \beta_3}{r} \right), \quad (\text{S13})$$

$$K_{10} = r \frac{b_1}{2\Delta} (1 + a_1 \Lambda), \quad 1 - K_{11} = \frac{1}{\Delta} \left(\beta_3 - a_2 b_1 \Lambda \frac{r}{2} \right), \quad (\text{S14})$$

$$r = \sigma_W / \sigma_i, \quad y_1 = \beta_6 / \beta_{12}^2, \quad (\text{S15})$$

$$\beta_3 = 1 + b_2/3, \quad \beta_6 = 1 - b_2/6, \quad \beta_{12} = 1 + b_2/12, \quad (\text{S16})$$

$$\Delta = \frac{b_1^2}{4} + \beta_6^2, \quad D_F = \frac{1}{2} \left[\beta_6(1 + b_0) - b_1^2 \frac{r}{12} \right], \quad \Lambda = \frac{1 + b_0}{2} + \beta_6 \frac{r}{6}. \quad (\text{S17})$$

Expressions for the electrostatic contributions to the chemical potentials read,

$$\beta \mu_i^{el} = \frac{L_0}{\sigma_i} b_0 - \frac{L_0}{\sigma_W} \frac{d_2}{d_0} b_1. \quad (\text{S18})$$

with $i = +$ or $-$ because $\mu_+ = \mu_-$ when the cation and the anion have the same size and charge in absolute value.

In Eq. (S18) the first term,

$$\beta\mu_i^{ii} = \frac{L_0}{\sigma_i} b_0, \quad (\text{S19})$$

is the contribution from ion-ion interactions to $\beta\mu_i^{el}$ (note that $b_0 < 0$), and the second term,

$$\beta\mu_i^{id} = -\frac{L_0}{\sigma_W} \frac{d_2}{d_0} b_1, \quad (\text{S20})$$

is the contribution from ion-dipole interactions. Therefore,

$$\beta\mu_i^{el} = \beta\mu_i^{ii} + \beta\mu_i^{id}. \quad (\text{S21})$$

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