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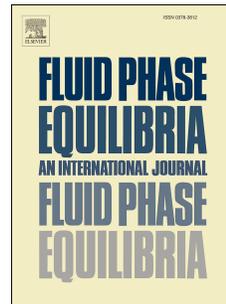
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The Debye-Hückel theory and its importance in modeling electrolyte solutions

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Abstract

A colleague at the Technical University of Denmark has often stated: “*Life is too short for electrolytes*”. Another well-known scientist in the field of molecular simulation has recently said during an international Thermodynamics conference: “*All my life I have tried to keep myself away from water and electrolytes*”. Sadly, what these statements correctly imply is that there are far too many unclear questions and concepts in electrolyte thermodynamics, and associated difficulties in modeling electrolyte solutions. In this work, we attempt to shed some light on some important concepts and misconceptions in electrolyte thermodynamics associated with the development of electrolyte equations of state, with emphasis on those based on the Debye-Hückel theory. Detailed mathematics is needed for some of the derivations but for brevity and in order to emphasize the principles rather than the derivations, the latter are omitted. We first discuss the peculiarities of electrolyte thermodynamics and associated modeling and continue with the derivation of the Debye-Hückel theory. The assumptions and limits of application of Debye-Hückel are discussed in particular. Next, the Born term and its significance and implications are presented in more detail. A discussion and outlook section conclude this review. Several of the statements in this work challenge “accepted beliefs” in electrolyte thermodynamics and, while we believe that this challenge is justified, we hope that a useful debate can result in improved and predictive thermodynamic models for electrolyte solutions.

1. Introduction

1.1 Importance of electrolyte solutions

Electrolyte solutions find numerous applications in physical sciences including chemistry, geology, material science, medicine, biochemistry and physiology as well as in many engineering fields especially chemical & biochemical, electrical and petroleum engineering. It is a huge field with vast literature and applications varying from the removal of CO₂ from flue gases of power plants, desalination of water, precipitation and corrosion in pipelines, oil production (scale formation, design of “smart water” enhanced oil recovery methods) to production of fertilizers and biotechnology (pharmaceuticals, protein purification). In all these applications, the thermodynamics plays a crucial role over wide ranges of temperature, pressure and concentration. Electrolytes (strong, weak, single or mixed) are present in solutions with water, sometimes also in other or mixed solvents. Understanding and design of the aforementioned applications relies on a variety of thermophysical properties, predominantly phase equilibria, but also thermal, volumetric and interfacial properties.

As the subject is important in many contexts and to many industries, large body of knowledge has been accumulated over the years with lots of experimental data and many models. For example, CERE, under the co-ordination of associate professor Kaj Thomsen, has compiled an extensive in-house electrolyte database¹ containing over 150,000 experimental data. Engineering practice today typically relies on suitable activity coefficient models, which are functions of temperature, often valid up to moderate electrolyte concentrations and containing many parameters fitted over extensive experimental data^{2,3}. These thermodynamic models are often useful in practice, typically tuned for specific applications and often have a rather weak theoretical foundation, although some of them are somewhat based on (some form of) the Debye-Hückel equation^{4,5} proposed almost 100 years ago by Debye (Nobel Prize, 1936) and Hückel. Due to the broad importance of electrolyte thermodynamics, it came as no great surprise when the EFCE (European Federation of Chemical Engineering) working party of thermodynamics and transport properties some years ago reported that electrolytes is the area where theoretical advances in thermodynamics and models based on theoretical foundations and of wide applicability are needed the most⁶.

Modeling electrolyte solutions is a very difficult task for many reasons, and not often well-described in textbooks, and typically only in textbooks dedicated to the subject. The first edition of the nominal work *Electrolyte Solutions* by Robinson and Stokes was released in 1955, followed by a revision in 1970 and 2002⁷. Zemaitis et al. published their Handbook of Aqueous Electrolyte Thermodynamics: Theory and Application in 1986⁸, which still serves as an excellent reference on activity coefficient-based models for aqueous electrolyte thermodynamics. Other important books in the field are those of Harned and Owen¹⁰⁸ and by Pitzer¹⁰⁹.

Often, other textbooks have not dedicated significant time to the subject, meaning that few students have been adequately exposed to the problems related to electrolyte thermodynamics. Only in 1999, 30 years after its first edition (1969), would Prausnitz and co-workers include a chapter on

electrolyte solutions in the 3rd edition of their well-known and widely used modeling book. In this chapter, Prausnitz et al.³ stated that thermodynamics of electrolyte solutions is a science of its own with differences from non-electrolyte thermodynamics being far from trivial. In their words “*It is a common misconception that extension of classical thermodynamics to electrolytes is only a small detail, a little perturbation, like adding a short tail to a big dog.*” and added that “*When two ions are e.g. 5 diameters apart, there is a strong interaction between them (the long-range nature of electrostatic forces). However, when two uncharged molecules are 5 diameters apart, one molecule hardly knows that the other one is there*”.

Thermodynamics of electrolyte solutions is a science of its own with significant differences from non-electrolyte thermodynamics. Whereas the SAFT theories have significantly improved predictions of neutral hydrogen-bonding compounds as well as aromatics, the many attempts of extending these good results to electrolyte solutions have yet to produce a fully predictive thermodynamic model for electrolytes, where the parameters must not first be estimated against mixture data.

The demands for a predictive electrolyte equation of state (EoS) are tough and depend greatly on the application. Moreover, there is an extremely wide range of applications, types of properties and conditions of interest, including activity coefficients (for the salts and the solvents), solubilities, mixed solvents and salts, volumetric & thermal properties and all the above over wide temperature ranges (not just around room temperature), often also at high pressures, for symmetric (e.g. NaCl) and asymmetric (e.g. Na₂SO₄) electrolytes, strong electrolytes (salts) and weak electrolytes e.g. acetic acid or ammonia, dilute and concentrated solutions and last but not least extensions to biotechnology (e.g. amino acids, peptides and proteins).

The neutral molecules forming weak electrolytes themselves pose difficulties for even state-of-the-art thermodynamic models and the modeling of the effect of pH requires knowledge of the equilibrium constants over wide ranges of temperatures and pressures, which greatly contributes to the difficulty of developing a predictive model – not only do you have to do well for components that are difficult to model even with the state-of-the-art thermodynamic models, you also have to account for other types of data and properties, as they can have a dramatic effect on the phase behavior.

Table 1 presents some of the most important data/applications of relevance to electrolyte solutions and some of the challenges associated with them.

Table 1. Some types of thermodynamic data of relevance to electrolyte solutions and challenges.

Data types	Conditions	Comments-Challenges
Mean ionic and osmotic activity coefficients, densities, solvent activities, vapor pressures, freezing point depression	Many data available over extensive T ranges, some also at high P (NaCl-water) Data available also for mixed salts-water	Classical data used by many model developers, but often only for 1:1 electrolytes and 25 °C Data available also for 1:2, 2:1, 3:1, 3:2, 4:1, 1:4 electrolytes
Salt solubility e.g. as molality against temperature (SLE)	Data available for diverse salts and over extensive T-ranges Some data also available at very high pressures as well (scaling) Data available also for mixed salts at various T Also for solubilities in mixed solvents e.g. water-alcohols, glycols Also some data for salt solubility in non-aqueous solutions e.g. alcohols	Very important data almost never considered in most e-EoS development Serious issues with the standard states definition and data
Gas solubilities in aqueous salt solutions incl. mixed salts (brine) –up to very high pressures	Data available for methane, nitrogen, CO ₂ , natural gas,...	
Hydrate dissociation curves (P-T)	Very extensive T/P ranges Mixed solvents e.g. water-alcohols, glycols + salts	
Heat of dilution (integral and differential), heat of solution	Data available for many salts	Rarely considered in model development
Heat capacity of brines and apparent molar heat capacity of salts	Data available for many salts	Rarely considered in model development
Hydration enthalpies of ions Heat of solvation of salts	Available data for many ions/salts	Rarely considered in model development
Solubility of hydrocarbons in aqueous salt solutions	Available data for many hydrocarbons	
Vapor-liquid equilibria of ternary solvent-salt systems	E.g. water-methanol-salt or water-acetic acid-salt or water-acetone-methanol-salt	
Liquid-liquid equilibria of ternary solvent-salt systems	E.g. water-propanol-salt or water-butanol-salt	Salt-induced LLE
Equilibrium constants of weak electrolytes in medium	E.g. CO ₂ in water or glycol	Limited experimental data available at high T, P
Density of salt solutions, apparent molar volumes of salts	Data available for many salts	Rarely considered in model development

From the perspective of the model development, the diverse types of properties that should be addressed from a model, is not an issue to be taken lightly. Development of a truly successful universal electrolyte model (e.g. EoS) should involve considering (either in the parameter estimation or the model validation) all the available data for electrolytes: water activity (vapor pressure, osmotic coefficients), mean ionic activity coefficients, salt solubilities, volumetric and thermal properties (heat capacities, heats of dilutions). All of these properties are needed for both single and mixed solvents and, ideally, over the whole temperature and molality (concentration) range available or of interest. In order to set the scene for a discussion on which diverse phenomena one must incorporate in a complete model, the next section takes a view on the wide range of complex phenomena that occur in electrolyte systems.

1.2 A brief overview of the complex phenomena in electrolyte solutions

Figure 1 shows the unsymmetrical activity coefficients of a classical water-ethanol mixture compared to NaBr in water or in ethanol. The activity coefficient of ethanol in water behaves in a much simpler fashion than the activity coefficient of NaBr in water and the non-ideal behaviour of the NaBr activity coefficient becomes even more prevalent in ethanol. It is, however, remarkable how well the Debye-Hückel model predicts the deviation from ideality in the low-concentration region in both solvents, and that is the main explanation for the successes of activity-coefficient approaches with a Debye-Hückel term based on e.g. e-NRTL, e-UNIQUAC, or Pitzer.

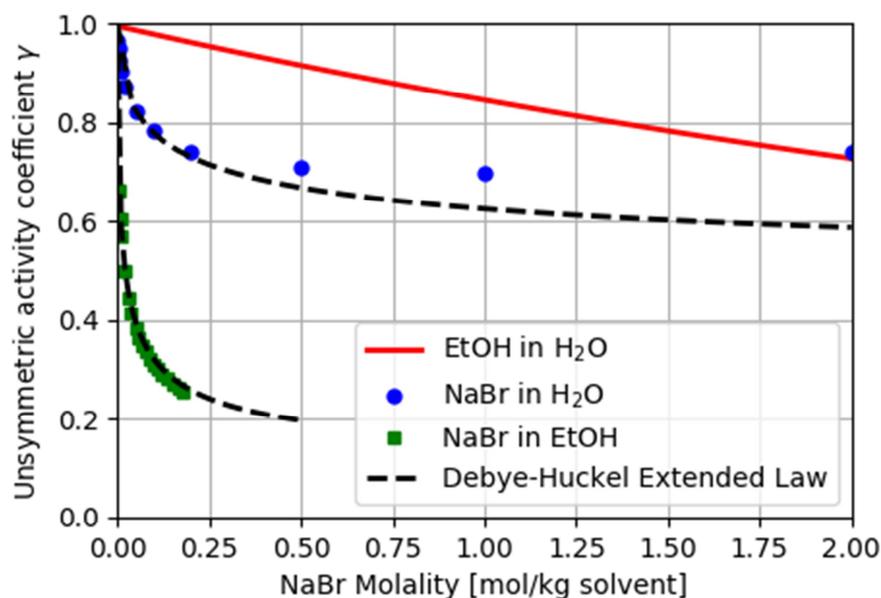


Figure 1: Unsymmetrical activity coefficient of ethanol in water (solid line), and activity coefficients of NaBr in water and ethanol⁹ at 25°C, 1 bar up to 2 molal (4 mol%) and comparison to predictions from the Debye-Hückel limiting and extended laws. Experimental data from Han and Pen (1993)⁹

One also observes a minimum in the activity coefficients of NaBr in Figure 1. Some (Frosch et al., 2010¹⁰) have stated that it is due to the effect of water and more specifically the change of water structure due to ions. Others (Heyrovská, 2000¹¹) have attributed it to the fact that even strong electrolytes may (only) partially dissociate, and thus there is presence of unassociated salt molecules in equilibria with the ions. Finally, others attribute it to a balance between electrostatic forces dominating at low concentrations and other effects e.g. physical forces which can start becoming significant at higher concentrations.

The static permittivity is responsible for the largest fraction of the change in initial slope between NaBr in water and NaBr in ethanol, as shown in Figure 1. The static permittivity is an intrinsic property of the medium that depends on the multipolar interaction and it can vary greatly with temperature, but depends on the composition of the medium and is furthermore affected significantly by the presence of salts.

While it is not so evident that strong electrolytes like NaBr and other salts may partially dissociate in a strong solvent like water there is evidence (also from conductivity measurements in water-1,4-dioxane from Bester-Rogac et al., 2000¹³) that in media of low static permittivities (and at high temperatures), partial dissociation is indeed happening leading to what today is often called “ion pairing”, which can have several forms, see figure 2. This is often attributed to or explained by the presence of ion-ion association.

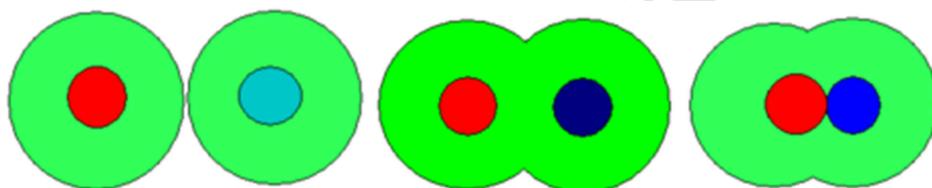


Figure 2. Ion Pair types: From left to right: SSIP (fully solvated), SIP (solvent separated), CIP (contact ion pair).

Recent evidence from EXAFS measurements¹⁴ have also revealed a significant degree of ion pairing in HCl-water even at 2.5 molal and at moderate temperatures, showing that the counter-ions cannot be assumed to merely act as spectators at higher concentrations, even in aqueous systems. Ion-pairing is, however, often neglected, as it complicates modeling efforts, and since the thermodynamic effects can be captured by fitting ion-ion interaction parameters in activity coefficient models – however, such treatments are empirical in nature and may lead to worse predictions and extrapolations.

Another problem posed by electrolyte systems compared to e.g. ethanol and water is that it is not trivial to obtain “pure” component experimental data. Typically, thermodynamic models will be parameterized against experimental data for vapor pressures, enthalpies of vaporization, and sometimes liquid densities of the pure compounds, but in the case of electrolytes these data does not exist, and thus we need to use mixture data like those shown in figure 3 (e.g. with water) to estimate

pure compound (salt or ion) parameters. As can be seen in figure 3, the temperature effect of various properties e.g. activity coefficients and solubilities can also be significant and requires parameterization of the thermodynamic model to temperature-dependent data – which may not always be available.

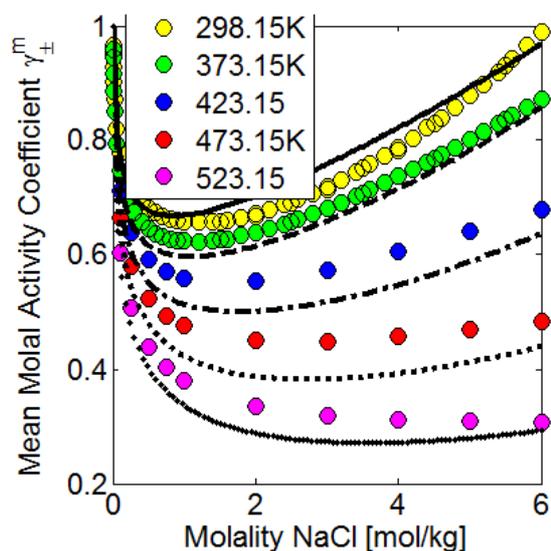


Figure 3. Temperature effect for NaCl solutions. Modified by Maribo-Mogensen¹². The calculations are made with an electrolyte CPA EoS using salt-specific interaction parameters.

Another aspect that is of great importance in modeling of electrolytes is solid-liquid equilibrium. The formation of solids is often unwanted, but can be quite complex to model accurately as it may involve both equilibrium and non-equilibrium reactions. For instance, in industrial boilers for steam, one typically finds scales made of silica, calcium sulfates, phosphates, and carbonates, magnesium hydroxides and phosphates as well as iron and copper oxides. Some can be highly problematic as they form hard surfaces on the inner surface of boilers and tubing, whereas others form powdery solids that can be removed downstream. To model each of these solids, one must have accurate thermodynamic data for the solubility constants or formation properties of the solid. The more ions that are present, the larger is the number of potential solids, and additionally, one also has to account for e.g. salt hydrates (such as $\text{NaCl}\cdot 2\text{H}_2\text{O}$, as seen in Figure 4).

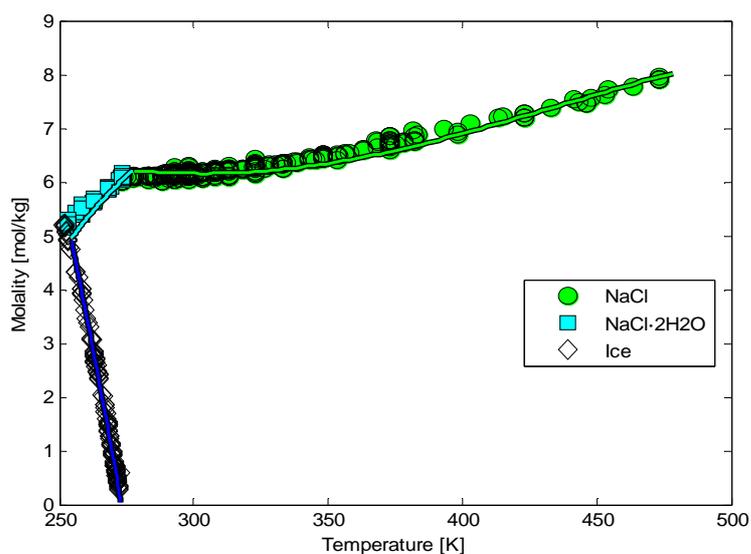


Figure 4. Temperature effect for salt solutions – salt solubility for NaCl. Modified by Maribo-Mogensen¹². The calculations are made with an electrolyte CPA EoS using salt-specific interaction parameters.

Many electrolyte problems also require accounting for weak electrolytes and this therefore necessitates accounting for e.g. acid-base reactions occurring in the liquid phase. The weak electrolytes are often in the form of trace components, which must be removed from gases (e.g. CO₂ and H₂S from natural gas or SO₂ from flue gas) before they can either be exported, converted, or emitted. In acid-base reactions, the speciation is mainly governed by the pH value, and as can be seen in Figure 5, the solubility of CO₂ may change by many orders of magnitude as a function of the pH.

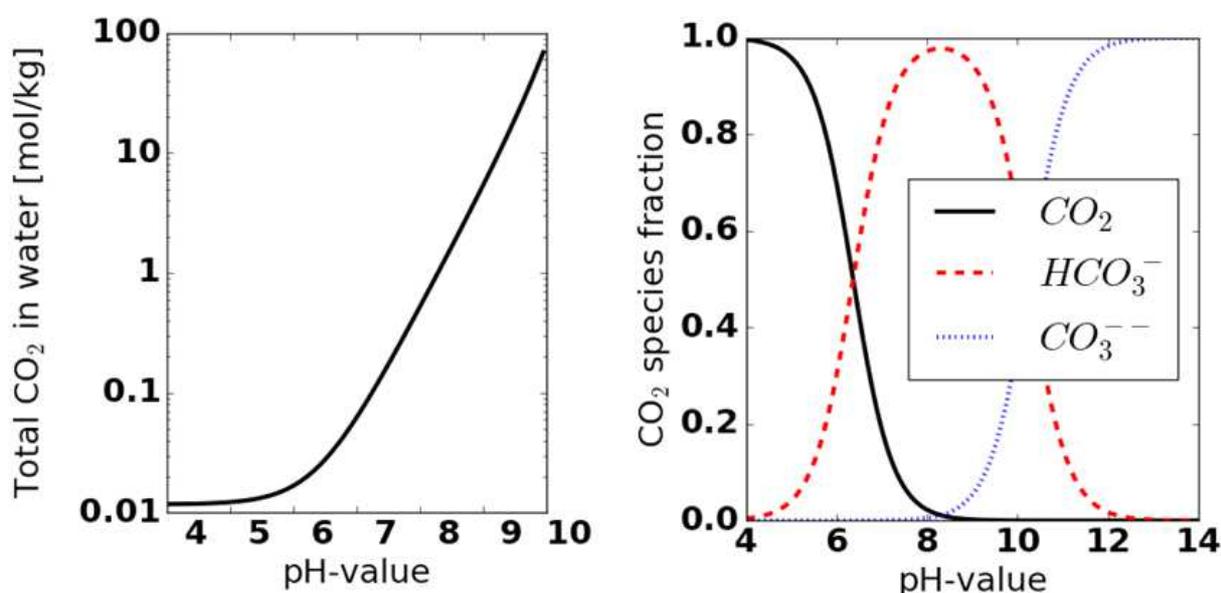


Figure 5: pH vs. total CO_2 in water ($CO_2 + HCO_3^- + CO_3^{2-}$) and the speciation of CO_2 in water at $25^\circ C$, 1 bar.

Weak electrolytes require knowing the equilibrium constants of all involved reactions as a function of temperature and pressure, which requires additional parameters and experimental data. Additionally, since the equilibrium constant depends greatly on the solvent, this can even have an effect for the behavior of strong acids (see Table 2). The thermodynamic model must be able to calculate the correct Gibbs energy of transfer from solvent A to B to accurately predict a correct equilibrium constant and speciation.

Table 2: pKa values for different acids in different solvents.

pKa	Gas	Water	DMSO	MeCN
HCl	328.1	-5.9	-2.0	8.9
HBr	318.3	-8.8	-6.8	5.5
HI	309.3	-9.5	-10.9	2.8
$HClO_4$	293.5	-15.2	-14.9	-
Acetic acid	341.1	4.76	12.3	23.51

The equilibrium constant can be difficult to model even for the simple reaction of $HCl(g) \Leftrightarrow H^+ + Cl^-$ in water, since it changes by more than 6 orders of magnitude when going from $25^\circ C$ to the critical point (Simonson and Palmer, 1993)⁷⁵. This is mainly due to the strong dependence of solvation free energy of the ions on the static permittivity and the weakening of hydrogen bonds in water at higher temperatures.

1.3 Thermodynamic modeling of electrolyte-containing systems

The diverse types of phenomena that must be modeled cannot be easily captured by a single model. Even if all of the physical phenomena are included explicitly in the model, it may still be possible to tune model parameters to capture the important behavior, at least for a limited temperature, pressure, and composition range. This has indeed been the philosophy of modeling of electrolyte systems until this day. Most practical engineering models are based on equations directly for the activity coefficients that are often extensions of well-established models from non-electrolyte thermodynamics (e.g. NRTL and UNIQUAC) by adding a suitable electrolyte term, often taken from some form of the Debye-Hückel theory^{4,5}. As we will discuss in the next section, the original formulation of the Debye-Hückel theory is not followed in these engineering-oriented (activity coefficient) models but typically some simplified form is used.

Capabilities and limitations of these models are described in the literature^{2,3,17} and Lin et al.¹⁸ recently presented a comparison of some of the most popular approaches. In this comparison of the Electrolyte NRTL (Aspen), Mixed-Solvent Electrolyte (OLI), and Extended UNIQUAC (CERE) 10 different test systems were modelled and while all models predicted VLE quite well, SLE calculations sometimes lead to incorrect speciation and solid phases. From this analysis it has been clear that validation of the model parameters against experimental data is required before using the activity coefficient models and the results with such models are highly dependent on the availability and reliability of the adjustable parameters, especially the interactions in the local composition part of the models.

A common characteristic of these activity coefficient models for electrolytes is that they need a large number of adjustable parameters which are fitted to a wide range of experimental data. They are useful in engineering practice within the conditions (esp. temperature and concentration) used in their development, but they cannot be easily used for extrapolations. They have a practical usefulness and as such are used in many industrial sectors. New applications almost inevitably require new data, and new regressions of parameters, and there are essentially no universal trends/links between the model parameters. These models lack generality and clear theoretical foundation, but they are very useful correlation tools (provided that considerable amounts of data are available), and they are used in engineering practice today.

A widely used alternative to the before-mentioned models are the Pitzer equations, which were investigated in a recent review from Rowland et al (2015)¹⁹, and will not be further discussed here. The Pitzer equations suffer from many of the same problems as the Debye-Hückel-derived formulations, especially with regards to an explosion in the number of adjustable parameters in electrolyte systems. The Pitzer equations also include an empirical modification of the Debye-Hückel term that reproduces the Debye-Hückel limiting law and can therefore be considered to be a Debye-Hückel derived model.

A new generation of electrolyte models has emerged very dynamically especially during the last 20 years in the form of electrolyte EoS (e-EoS in brief), see figure 6, developed either based on the primitive or the non-primitive framework. Unfortunately, there is currently very little

collaboration between the major research groups working with the two frameworks. Recent reviews of e-EoS have been published^{2,12,20-21}, while new e-EoS appear continuously. There are some interesting developments, some exciting results and progress is being made, but at the same time there is very little consensus in the scientific community on what has been really achieved and how to proceed.

The research community is divided quite sharply into two groups with limited interaction; those advocating the non-primitive approach²²⁻²⁵, fig.6-right, where water (solvent) is treated as a (dipolar) molecule interacting directly with ions, and the –currently- many more who support the primitive approach, with water being a dielectric continuum, fig.6-left^{2,12,18-21,26-44,46} where the solvent (e.g. water) is considered to be a dielectric continuum characterized by its static permittivity (relative static permittivity) ϵ_r .

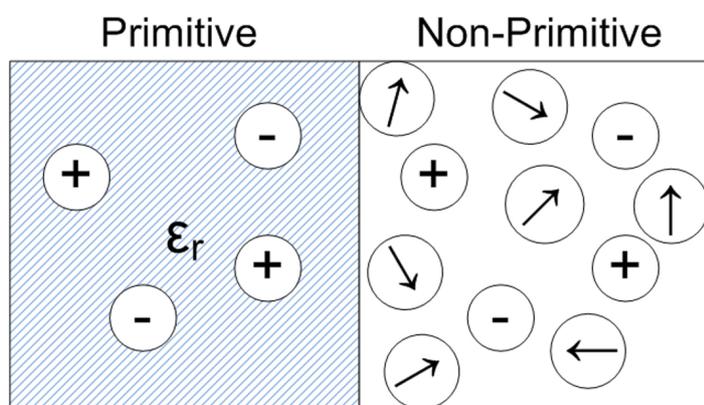


Figure 6. Fluid representation in the primitive (left) and the non-primitive (right) models for the electrostatic interactions. From Maribo-Mogensen¹².

“Non-primitive” supporters claim that this is the correct way of modeling electrolyte solutions, as all intermolecular interactions can be accounted for and that the microscopic nature of water is, in principle, “lost” in the primitive models, as water is not considered to be a molecule but a medium where the ions interact. In the non-primitive models, there is no need for using the static permittivity as input, and water’s (solvent’s) molecular character is important at short distances (high concentrations). Dipole-dipole interactions are explicitly accounted for and such models are much more complex compared to those based on the primitive approach. There have been some promising results with the non-primitive approach, especially by the groups of McCabe²² and Gross²³ but these developments are in their infancy at least from an engineering EoS point of view.

Supporters of the primitive approach believe that this is the only realistic way to arrive to an engineering approach which, with few parameters, can yield useful results in practice. And as these primitive theories are indeed widely used, inevitably, differences occur between the various primitive approaches which are far from trivial. These fundamental-in-nature differences can affect development and results. In the following sections, we will go through some of the literature on electrolyte EoS and present some of the major questions that still face new and old researchers in the field; basically, how do we create the ultimate electrolyte EoS that will capture all of the phenomena? Do we need all of the terms shown in Figure 7?

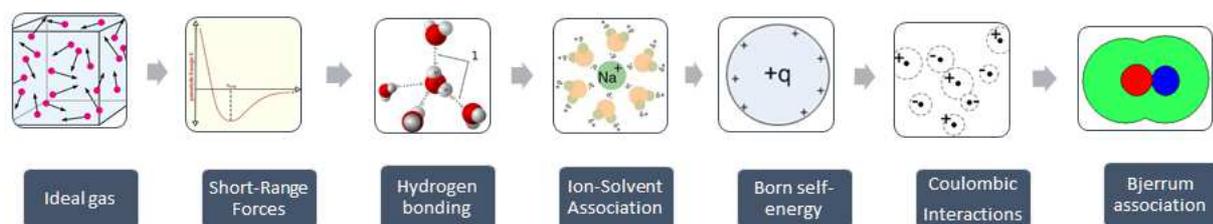


Figure 7. Contributions to (the Helmholtz energy form of) an electrolyte EoS. In addition to contributions from physical and chemical (hydrogen bonding) forces, such models include various contributions to electrostatic (Coulombic) interactions, possibly also including effects from ion-solvent and Bjerrum associations (ion-pairing). From Maribo-Mogensen¹².

In this manuscript we would like to investigate some of the major discussion points and look at the following important questions:

- Theory:
 - Which model should be used? I.e., which physical & electrolyte terms? primitive or non-primitive?
- Model development:
 - which parameters should be fitted?
 - how many parameters should we fit?
 - what experimental data should be used in the fit?
 - what is the sensitivity of the results and flexibility of the model?
- Model validation:
 - which properties should be tested?
 - which concentration, pressure and temperature ranges?
 - how easily extended to other situations including mixed solvents and mixed salts
- What are the true model capabilities and limitations?
 - what is hidden and/or what is not being said?

We will begin this by a review of electrolyte EoS in literature to illustrate some of the different approaches researchers have taken to come up with a general electrolyte model.

1.4 Review of recent electrolyte EoS

Primitive-based models

J.M.Prausnitz has led several efforts in the e-EoS field, with Simon²⁶ using cubic EoS for the physical term (1989, 1991) and with Wu²⁷ using CPA in 1998. In the latter model a Born term is used together with an empirical expression for the concentration dependency of the static permittivity. All models have been used for very few systems and for only gas solubilities (salting-out) calculations. In their e-CPA approach they used water-ion association, not used in any of the other e-CPA models. The very few calculations shown for a very limited range of systems and conditions, and using several adjustable parameters, do not permit any thorough appreciation of the approaches. More interesting is the article with Simon in 1991²⁶ where mixed solvents are

considered and where an analysis of the term of the EoS (see previous section) is presented. None of these approaches have been further developed by the same or other researchers towards more demanding applications e.g. at high temperatures, salt solubilities and LLE calculations.

The Furst and Renon (1993)²⁸ e-EoS is the first electrolyte EoS based on a cubic EoS for the physical term. There have been several follow-up articles in 2000-2002 and the model has been extensively used for binary and ternary (osmotic) activity coefficients at 25°C and also mixed salts, hydrates, mixed solvents VLE & LLE incl. non-aqueous systems (e.g. by Vu et al.²⁹ and Zuo et al.^{30,31}). The results are satisfactory with few adjustable parameters and can be improved if the cation-anion interaction is fitted. However, the authors have never considered high temperatures and SLE (salt solubilities). Another salt-based e-EoS proposed by Myers-Sandler-Wood (2002)³² which has been used over an extensive T-range, up to 300°C, is shown to only give good results when three salt-specific parameters (energy, co-volume, diameter) are used and all three are T-dependent and an additional interaction parameter k_{ij} for water-salt is used. The model's application has been limited to 140 water-single salt systems. None of these two models have ever been developed further as ion-specific models.

Lin et al. (2007)²¹ also published an electrolyte version of CPA. They considered mixed salts and SLE and they noticed a huge effect of data used on parameter estimation. If a wide range of data should be reproduced (mean ionic and osmotic activity coefficients, volumes, and SLE), a large number of adjustable parameters are needed. Without SLE data, the ion-ion and cation-water interaction parameters and fitting the diameters can be eliminated and, if in addition, no volumetric data are used all energy interaction parameters can be eliminated.

In the group of de Hemptinne in France both e-CPA (Inchekel et al., 2008³³; Courtial et al., 2014³⁴) and e-PC SAFT (Rosmus et al., 2013³⁵) have been used in various publications with different modeling approaches. Comparisons of the two models are not shown, applications also differ, but we suspect no significant differences if the same parameter estimation procedure would have been followed for both models. In all cases a Born-term with an empirical concentration-dependent static permittivity expression is used. There are no SLE results (salt solubilities) in any of the works but as one of the few studies in the 2013 article (Rosmus et al.³⁵) are reported results at high temperatures and salting-out calculations, with a modest number of temperature-independent adjustable parameters. It is clear that activity coefficients reported at high temperatures are not in good agreement with experiment. This is also one of the few recent studies discussing the importance of ion pairs in electrolyte modeling. De Hemptinne and co-workers³⁵ conclude that without considering ion pairs, poor activity coefficient results should be expected at high temperatures and molalities above three (including salting-out over wide temperatures).

Two research groups which have presented extensive results for electrolytes in a series of publications are those of professors Sadowski (Dortmund, Germany) and Jackson-Galindo (Imperial College, UK).

The work of Sadowski, Held and co-workers on electrolytes started with the first articles published in 2005 (Cameretti et al., 2005)³⁶ but there have been numerous articles since then³⁷⁻³⁹. Their model is based on an e-PC-SAFT using the full DH model and no Born term. There is good agreement for both vapor pressures and liquid densities up to 5-20 molal (for over 100 single salt-water systems), and even activity coefficients, but only when the latter have been included in the parameter estimation. The fitted parameters are ion segment energies and ionic ("hydrated") diameters which seem to have reasonably correct values. The interest of this group is for biological applications (amino acids, peptides, ...) and all results are reported at 25°C and no test at higher temperatures is reported. No SLE results are shown either, but recently³⁹ successful results have been reported for ternary activity coefficients and densities of mixed salts and mixed solvents (water-alcohols), all at 25°C, as well as water-salt-amino acids. Ternary LLE results have been reported for a few systems (water/NH₄Cl/butanol), Held et al., 2014³⁹, but now a new approach is used including also cation-anion and ion-alcohol interaction parameters fitted to the ternary data. This approach "mimics" ion pairs at high salt concentrations without using extra terms. These results are only partially successful and they are not predictive.

At Imperial College, Jackson, Galindo and co-workers have been using since 1999 electrolyte EoS based on MSA and various versions of SAFT in the physical term. Early results until 2003^{40,41} were limited to VLE and densities for a few water-salt systems (at various temperatures) and salting-out curves (and a collaboration article including alcohols-salts and activity coefficients up to 20 M), as well as gas hydrates with salts. These rather simple calculations only required fitted ion-water dispersion parameters and the Pauling diameters were used. No activity coefficients, SLE or mixed solvents were considered until 2003.

Much more impressive results are presented in two recent articles in Molecular Physics (2014, 2016)^{42,43} using the SAFT-VR Mie as model for the physical interactions and a Born term is now included in both recent articles^{42,43}. Densities, water activities activity coefficients up to high molalities and temperatures (limited studies at high temperatures), freezing-point depression curves are considered as well as Gibbs energy of solvation and even mixed salts including brines and mixed solvents. The results are satisfactory at room temperatures, but not very accurate at high temperatures and high salt concentrations and no SLE/salt solubilities are considered either. LLE for a single system (water-butanol-NaCl) is presented. These are excellent articles and two of the most thorough recent investigations. It remains to be seen whether the SAFT-VR Mie model for electrolytes can find a more widespread use in terms of properties and applications.

Is Debye-Hückel only valid at low concentrations?

A few authors state that overall MSA should be preferred to Debye-Hückel (see references in Kontogeorgis and Folas, 2010² and Maribo-Mogensen et al., 2012⁵⁶). For example, Myers, Sandler and Wood 2002³², have stated that Debye-Hückel performs worse than MSA, especially at high concentrations. Other researchers (Galindo et al., 1999⁴⁰; Patel et al., 2003⁴¹) have commented that MSA yields better agreement with liquid densities than DH, but this in reality would depend on the value selected for l_i .

In reality these statements have been made in literature essentially without proof and without really comparing the two theories. The superiority of MSA over DH has thus become almost an

“established” fact without a shred of proof. Several researchers (see references provided by Zuckerman et al., 1997⁹²) have stated that MSA may not be superior to DH even from the theoretical point of view; it has been demonstrated that the DH theory yields pair correlations satisfying the Ornstein-Zernike relation in a very natural way.

From the practical point of view, Lin (2007)⁹³ illustrated that MSA and DH yield almost identical results at the “common ion size” limit (restrictive primitive approach).

A more systematic comparison of the two theories has been carried out by Maribo-Mogensen et al. (2012)⁵⁶ who compared the two models in terms of the results for the Helmholtz energy and its first order derivatives with regards to temperature, volume and composition.

The major conclusion from this work is that MSA and the Debye-Hückel models were found to perform similarly (in terms of the reduced Helmholtz energy) if the Debye-Hückel distance of closest approach parameter was set to 5/6 of the MSA diameter.

It was also shown in the same work that the static permittivity is the most important parameter which influences the electrostatic interactions. It was emphasized that the static permittivity and its concentration dependency are actually a much more important parameter than selecting MSA or DH for the electrostatic interactions. It was further demonstrated that using an empirical model for the static permittivity may introduce possible unphysical behavior into the EoS, which can greatly influence equilibrium properties. It is, thus, of paramount importance to use either the DH or the MSA theories coupled with a theoretically-sound model for the static permittivity.

An additional confusing factor comes from statements in established books of statistical thermodynamics^{57,58} where the general DH expression is indeed mentioned with the additional comment that it should not be used due to the assumptions in the derivation, especially the underlying use of the primitive model and non-molecular character of water. We object to this way of thinking, because, while there are indeed assumptions also in the general DH equation, its actual range of applicability has not been fully appreciated or evaluated, as this should be done only by testing the assumptions and, from the practical point of view, by combining the DH equation with other contributions for the physical forces in a complete model for electrolyte solutions. The argument is also problematic since the primitive MSA model makes most of the same assumptions, except from including a short-range repulsive term, which does not appear to greatly change the representation of the Helmholtz free energy, as shown by Maribo-Mogensen et al. (2012)⁵⁶.

Non-primitive modeling approaches

In all studies of non-primitive models²²⁻²⁵, a non-primitive version of the MSA for ion-ion interactions is combined with suitable ion-dipole and dipole-dipole terms and a physical term, often from some SAFT variant. Earlier efforts^{24,25} have shown that the results were dependent on the static permittivity (and whether it should be that of water, function of salt concentration, etc) and often the non-primitive nature of the model had to be violated by introducing the static permittivity as input to the model.

A difficulty in developing successful non-primitive models for electrolyte solutions lies partially in the fact that it has not been clearly demonstrated how we can develop successful SAFT-type models for mixtures with dipolar and associating fluids e.g. water with alcohols by explicitly including also

dipolar terms. Dipolar versions of SAFT have been proposed but are only partially successful for such mixtures.

Nevertheless, the work by Herzog, Gross and Arlt²³ was a genuine effort towards a truly non-primitive electrolyte EoS for engineering applications. Some promising results were shown but for very few applications (just activity coefficients) but there has not been any follow-up from this research group. Nevertheless, this is one of the few studies where activity coefficients up to $m=20$ are presented for a few salt solutions.

An even more interesting and complete work presented by Das et al.²² has been mentioned in section 1.2. For the first time ever with a non-primitive approach, static permittivities as output are presented in qualitative (but not in quantitative) agreement with salt concentration. These values depend a lot on both temperature and the exact input value used for the dipole moment of water. One further message from this study is that while satisfactory results are obtained to molality of around 6 and low temperatures, good agreement at high temperatures and high molalities need explicitly accounting either for ion association (ion pairs) or (an)ion-water short range interactions. Such problems had been seen also with the primitive approach but these were then attributed to the “primitive” nature of the model (where e.g. solvent-ion interactions should be captured just by the static permittivity of water). From the work of Das et al.²², we clearly see that the non-primitive approach has similar problems. Moreover, the “solution approach” presented for high molalities is not universal, as salts with symmetrical ions e.g. LiCl are prone to give ion pairs, while those with asymmetric ions e.g. LiBr are completely dissociated even at $m=12$. However, both types of salts have problems at high molalities, thus the need for the two different “solution approaches” mentioned above. We put the word “solution approaches” in quotations, as not only are they not universal at high concentrations but they require additional adjustable parameters (e.g. an empirical extra term for ion pairing), some even salt-specific. So, it is not clear whether the improvement is partially due to the additional adjustable parameters.

Both Gross and McCabe works^{22,23} presented results for the Gibbs energy of solvation for different ions and salts. The results are rather satisfactory and reported to be better than some of literature studies with primitive models e.g. vs. from Imperial College study⁴² (12.5% deviation in the Gibbs free energy of hydration of 19 salts vs. about 50% for 8 ions in ref.⁴²). Better Gibbs energies of solvation would indeed indicate some superiority of the non-primitive approach which has an explicit ion-solvent term, but recent extensive comparisons of the Gibbs free energy of hydration for several salts⁴⁴ clearly contest this argument and show no superiority of the non-primitive over the primitive approach, possibly indicating that even for this property good agreement may be more due to fortunate parameter estimation. For 8 salts, in ref. 44 is reported a 6.4% deviation in the predicted Gibbs free energy of hydration with their primitive e-SAFT + Born model vs. 11.5% with the non-primitive approach of Das et al.²² for the same salts.

Moreover, in the more recent publication by Imperial College⁴³, the average percentage deviation for the free energy of solvation of 13 ions is about 4% with the SAFT-VR Mie model which is also a primitive approach. The improved results are attributed to using different diameters in the Born and electrostatic terms in the latter model (Born diameters taken from Rashin and Honig⁴⁵). Thus, any superiority of the non-primitive approach in describing Gibbs energies of solvation is rather unclear (at best) or non-existent. In another manuscript⁴² they mention that non-primitive model

approaches with explicit ion-solvent interaction terms should perform better than primitive approaches for solvation energies (but this is contested by others).

Finally, it is worth mentioning the comparison between non-primitive (ion-ion from MSA, ion-dipole) contributions and the corresponding primitive terms (Debye-Hückel and Born) shown by Maribo-Mogensen¹². There are non-trivial differences between the two approaches, especially at high molalities and in the derivatives wrt temperature and volume, but overall there is reasonable agreement between the chemical potential from the DH model and the npMSA, once a physically correct model is used for the static permittivity. The model for static permittivity plays a significant role in these calculations and results are sensitive to the equation used for the static permittivity of the solvent.

The effect of ion-solvent association

Robinson and Stokes (1948)⁷ derived a model for the effect of ion hydration on the activity coefficients using considerations of the Gibbs-Duhem equation. They showed that the activity coefficient with ion hydration was related to that without through:

$$\ln \gamma_{hyd}^{\pm} = \ln \gamma^{\pm} - \frac{n}{\nu} \ln a_w - \ln(1 - nM_w m^{\pm})$$

Where γ_{hyd}^{\pm} is the observed mean ionic activity coefficient with ion hydration, whereas γ^{\pm} is the mean ionic activity coefficient without ion hydration (i.e. Debye-Hückel), n is the number of hydration sites on the salt, ν is the stoichiometric coefficient of the salt (i.e. 2 for 1:1 salts), M_w is the molar weight of water and m^{\pm} is the molality of the salt. They used the osmotic coefficients to evaluate $\ln a_w$ and through this very simple model, Robinson and Stokes could show that the hydration numbers of water could be fitted to higher concentrations using realistic hydration numbers for the salt (0.6-20). Unfortunately, a complete generic thermodynamic model cannot easily be built on the above equation, as it does not account for mixtures or mixed solvents, but it showed the potential importance of accounting for ion hydration.

Several groups have included the effect of ion-solvent association in an EoS, e.g. through the Wertheim framework. Here, researchers disagree on the number of association sites which should be used for ions. An interesting recent discussion which includes a table summarizing the association sites adopted by 5 models is provided by Rosmus et al.³⁵ One would have expected that such association sites should be somewhat related to the hydration numbers of ions but only rough correspondences exist. Hydration numbers are typically 4-6 for the more hydrated cations and lower for the anions. With the exception of Wu and Prausnitz²⁷ who assign very high values of association sites in their e-CPA (10 for Na⁺ and 14 for Cl⁻), in most models the association site values range between 6-8, with cations around 7-8 and somewhat lower for anions. Rosmus et al.³⁵ also showed that with increasing ion concentration, hydrogen bonding decreases and thus we do have a disruption in water structure. These conclusions are based on calculations with their thermodynamic model (thus should be taken with some reservation). Other researchers have stated that ions play a significant role on water structure (Frosch et al., 2010¹⁰), while others disagree (Omta et al., 2003⁴⁹).

Maribo-Mogensen et al. (2014)^{47,48} developed a physical model for the static permittivity that included the effect of ion hydration and predicted the decrease in the static permittivity using hydration coordination numbers of 5 for anions and 7 for cations, and investigated the effects on the Debye-Hückel term. This was also compared to the npMSA model¹², and it was shown that if this effect on the static permittivity was included, one would recover some of the characteristics of non-primitive models. This model was investigated further by Shahriari and Dehghani (2017)⁴⁴ in their e-PC-SAFT, who also obtained good results for apparent molar volumes.

What is the effect of the Born term?

It is interesting that, despite its “apparent” importance, the Born term had been ignored in most electrolyte EoS for many years, possibly because the static permittivity was considered to be independent of concentration. In the recent years, the use of Born term in e-EoS has become quite popular and several approaches within the primitive framework (e-PR by Myers et al.³², e-CPA by Maribo-Mogensen et al.⁴⁶ and Schlaikjer et al.⁵⁰, e-SAFT VR-Mie by Jackson, Galindo and co-workers^{42,43}, PC-SAFT by de Hemptinne and co-workers^{33,35}, and by Shahriari and Dehghani⁴⁴) as well as the non-primitive approaches by Das et al.²² and Herzog et al.²³ are using it. In some of these studies, hydration enthalpies and Gibbs free energy of solvation calculations are presented for several salts which are found to be in reasonably good agreement with experimental data.

In some of these studies it is stated that the magnitude of the Born term is as significant as of the electrostatic interaction (either given by the Debye-Hückel or by MSA), and of opposite sign, and thus this term can simply not be ignored as discussed by Inchekel et al. (2008)³³, Simon et al. (1991)²⁶ and very recently by Shahriari and Dehghani⁴⁴ who all showed that the contribution of the Born term to the activity coefficient is of same size but opposite sign as the Debye-Hückel or MSA contributions. This leads to two terms almost canceling out in the liquid phase.

Despite this, we have seen in literature e-EoS either totally ignoring the Born term or using different descriptions of the static permittivity in the Born term than in the Debye-Hückel term. We believe that the inclusion of the Born term with an appropriate concentration dependence of the static permittivity (and identical to the model used in the Debye-Hückel term) appears to be important in the development of reliable and consistent electrolyte EoS. Failing to do that, may put “too much pressure” on the fitting parameters and procedure of e-EoS which are based e.g. only on the DH term.

For instance, Inchekel et al. (2008)³³ compared the contributions from Born and MSA terms in the e-EoS they developed and they find that the positive Born contribution almost counterbalances the MSA contribution and conclude that the Born term has an important effect, while other terms in their e-EoS are less significant. They also comment that if the composition dependency of the static permittivity (and thus the Born term effect in activity coefficients) is ignored, then the other terms

of the EoS should counterbalance the MSA effect in order to obtain the correct activity coefficient slope at high salt concentrations.

Finally, many results (e.g. Maribo-Mogensen¹²) clearly indicate that the Born model is required to capture a high driving force for the ions towards the polar phase, and is therefore crucial for accurate description of the vapor-liquid-liquid phase equilibrium in the oil-gas-brine system. The importance of the Born energy in determining the extent to which ions will dissolve and partition in different solvents has been emphasized by many authors (e.g. Israelachvili, 1985⁵¹). Thus, the Born term (for the energy of hydration) provides the dominating driving force for keeping the ions in the polar phase, ensuring that they do not enter the oil or vapor phases, making it crucial for oil-water equilibrium calculations. This further emphasizes that the Born term cannot be ignored in thermodynamic calculations.

The Born term may have a special significance also at high concentrations. Indeed which effects are dominant at concentrated electrolyte solutions is still debated. As previously mentioned, ion-pairing effects can be very important (due to partial dissociation) but short-range physical interactions may also be important in these cases. It is unclear whether the importance of physical effects at high concentrations can mask the ion-pairing effect. Even above 0.1 M, it has been reported that physical interactions can be important. While the exact balance of the various effects has not been systematically studied, not even via molecular simulation, the Born and ion-hydration effects especially with a concentration dependency of the static permittivity may partially account for these effects.

In a somewhat different note, Shahriari and Dehghani⁴⁴ does present excellent results with an e-SAFT primitive approach for diverse properties including heat capacities as function of temperature. A Born term is included as well as sites are assigned to ions (6 for cations and 5 for anions). They do emphasize, and this is similar as the Imperial College works^{42,43}, the huge importance of using the Born term with a physically correct static permittivity expression, also function of concentration and using diameters higher than the ionic diameters for both cations and anions. Born's role in improving the derivative properties is very important. They do present excellent solvation energies, actually better than previous approaches including the non-primitive method of Das et al.²² While good solvation energies and structural properties (C_p over extensive temperature and concentration ranges) representation are indeed very interesting results, the molality range is rather limited, as can be seen by both the few activity coefficient and the few SLE results shown (figures only showing results up to 2 mol/kg, and tables up to 6 mol/kg).

In conclusion, we should expect that when the static permittivity is constant and independent of concentration, then the contribution of the Born term will be very small (zero) to the chemical potentials and activity coefficients, but if the concentration dependency is considered, including mixed solvents, the Born effect could be quite significant.

None of these statements have, as yet, found widespread acceptance in the scientific community and in some sense it is interesting that these topics are discussed almost 100 years after the publication of the Debye-Hückel and Born equations, in 1923 and 1920!

What is the effect of ion-ion association?

While Maribo-Mogensen¹² advocated the use of additional terms e.g. Bjerrum or some form of Wertheim theory for accounting for the ion-ion association effects, most researchers have attempted to include these contributions within their existing e-EoS approaches by adding more parameters or concepts.

Ion pairs have been accounted for, in the non-primitive context, with two different approaches by Rosmus et al.³⁵ and Held et al.³⁹.

Rosmus et al.³⁵ emphasize the use of ion pairs at both high temperatures and high molalities, even above $m=3$. Their model is an e-SAFT with MSA and Born, which accounts for the electrostatic part of ion-water interactions. The short-range (SR) water-ion interactions, i.e. the non-electrostatic part, are accounted for via sites for ions with the water-ion association energy being adjusted. Thus, their concept is to account for ion pairs via ion-ion association using the Wertheim theory instead of considering dispersion interactions (as Held et al. did³⁹, see below). Ion-ion and water-ion dispersions are neglected, only association is considered between ion-water and ion-ion. Ion pairs are described via these cation-anion associative interactions, mimicking the cation-anion aggregation. Problems related to assigning sites to ions were discussed above. Despite having considered the ion-pair effect, results are shown only up to $m=6$, no SLE is presented and we see serious deviations at high temperatures. The rather significant deviations for density may be due to the fact that the diameter has not been fitted to experimental data. Association between cations and ions (Na^+/Cl^-) was also used by Wu and Prausnitz²⁷ in their e-CPA but the applicability of this model to just one system (NaCl +water and ternary with methane) is very limited to get any final conclusions, even though temperatures up to 300 °C were considered.

A different approach to account for ion-pairs is via dispersion by introducing short-range forces between ions. This has been followed by Held et al.³⁹ who proposed recently a new strategy for their e-PC SAFT which does not include a Born term. Their previous approach which was sufficient for activity coefficients up to $m=6$ (for many salts) only included an ion diameter and ion segment energy fitted to data. This previous approach was found insufficient for high concentrations where ion pairs may exist and for weak electrolytes. In addition to these parameters, their recent new strategy includes a k_{ij} between ion-water, k_{ij} 's between cations and anions (and k_{ij} between ion and other solvents as well). These k_{ij} parameters permit the model to account, in the “dispersive approach” for ion pairs, permitting good results up to higher molalities (up to 6). No high temperatures or SLE are shown. The LLE for water-salt-hydrocarbons and water-salt-butanol does illustrate that this approach is not an entirely optimal way for accounting for the ion pairs which indeed may have an important role in the mixed solvents as well (due to lowering static

permittivity). In all cases for ternary LLE, one or more additional k_{ij} parameters are needed which are directly fitted to ternary LLE data.

In the two recent manuscripts by Imperial College^{42,43}, ion pairs and ion-water association are not accounted for, at least not explicitly. The authors are aware of the importance of ion-pairs at high concentrations and they limit their model's application to lower concentrations but they are uncertain on which is the "maximum molality" that should be used for model development and validation. In the first manuscript⁴² the maximum molality is considered to be 10 (for parameter estimation), implying that after this limit the primitive approach breaks, partially due to ion pair creation. In the second manuscript⁴³, the maximum molality is 3 for parameter estimation and 6 for model validation (implying ion pairs at higher concentrations). The significant problems seen at high temperatures and high molalities including the SLE calculations are attributed to the failure of the primitive model approach at these extreme conditions.

Should we convert between Lewis-Randall and McMillan-Mayer frameworks?

When we develop a (primitive-based) electrolyte EoS, we combine short-range terms with long-range contributions based on the primitive theory (DH or MSA), where the solvent is considered to be a continuous medium characterized by its static permittivity, rather than a component. When we combine ("add") these contributions, several researchers have noticed the apparent inconsistency as we combine two different frameworks with different independent variables: the Lewis-Randall (LR) framework (independent variables = T , P , mole numbers of all species) for the short-range interactions with the McMillan-Mayer (MM) framework (independent variables = T , V , mole number of solute, chemical potential of solvent) for the long-range interactions.

Haynes and Newman⁹⁶ determined that the conversion from LR to MM resulted in the derivation of Debye-Hückel not giving an expression for the Helmholtz energy, but rather an excess term $A' = A - n_0\mu_0$, which should give rise to an excess pressure in the Helmholtz free energy and later also investigated this for mixed solvents. Breil and Mollerup⁹⁷ disagreed in their similar investigation about the differences between the two frameworks, and showed that the conversion between the two frameworks was superfluous when formulating the model in terms of the Helmholtz free energy as function of temperature, volume, and composition.

A few researchers are proponents of conversion of thermodynamic properties from MM before being added to short-range terms, expressed based on the "ordinary" LR framework. But how important are these conversions from the practical point of view? It is hard to tell. Prausnitz et al.³ mention that for single solvent-salt mixtures, the use of the different frameworks does not affect significantly the calculations, but care should be exercised for mixed solvents. In most electrolyte EoS developed so far, such corrections have been ignored or it is considered that they may be absorbed in the adjustable parameters (present in all models). Sandler and co-workers³² have commented on the small significance of the MM vs. LR frameworks for calculations while in their

e-CPA Wu and Prausnitz²⁷ did include corrections, but they offered no comparisons of the results with and without these corrections.

Which standard states should we use for solid-liquid equilibrium calculations

Considering how many electrolyte EoS have been developed, it is almost amazing how few studies present results for solid-liquid equilibrium calculations i.e. for salt solubilities in single or mixed salts in aqueous solutions. Such data are available for many salts over extensive molality and temperature ranges. A reason for the few studies could be that salt solubility calculations provide a very difficult test for models due to the extended conditions in terms of concentration and temperature (sometimes also pressure). However, there is an additional difficulty. Such calculations require data for standard state properties (Gibbs, Enthalpy and Cp) of the investigated solid salts. Such data are scarce especially for the hydrated salts and such properties should, thus, be considered as additional adjustable parameters for the models which have to be estimated together with the remaining parameters.

As Schlaikjer et al. 2017^{50,52} have noticed satisfactory correlation of both activity coefficients and salt solubilities required that both data are included in a simultaneous parameter estimation of the model parameters (e-CPA in that case). We suspect that a similar approach may be needed for most models and thus models (e-EoS) with parameters estimated by ignoring salt solubilities may not perform satisfactory for SLE. Unfortunately, this adds new parameters and essentially makes the model correlative for SLE, rather than predictive – in order to be fully predictive, we need a better model for the solid state or standard state properties of e.g. salts and salt hydrates.

Can we get input from molecular simulation data?

There are many fundamental questions in electrolyte thermodynamics and many had hoped that molecular simulation could provide significant input. It is now rather well-established (Panagiotopoulos invited lecture during the 2017 ESAT conference) that only limited research on molecular simulation for electrolytes has been carried out, especially for activity coefficients. Several recent studies by Panagiotopoulos group^{53,54} have shown that classical molecular water models show some mostly qualitative agreement for the activity coefficients of NaCl-water up to low molalities but there are significant deviations at $m > 3$. When results are extrapolated to salt solubility even worse predictions are obtained. Even more challenging is the temperature effect of salt solubility which only some models can correctly predict the increasing with temperature trend. Predicting wrong temperature-trends for these properties is clearly a serious problems indicating that fundamental improvements are needed.

According to Panagiotopoulos and others the future lies on polarizable water models and there are some promising but not fully conclusive results. It remains to be seen which among the many polarizable models will perform better and also whether improved results can be obtained over extensive concentration and temperature ranges. Another issue is that in these molecular models,

the static permittivity is an output, as in non-primitive approaches and, thus, the results can be highly dependent on the quality of static permittivity values produced, including their temperature dependency. Some of the observed limitations in predicting the solubility and activity coefficients at high temperatures may indeed be due to the static permittivity values predicted at high temperatures.

Molecular simulation studies have provided some insight and they indicate that decreasing static permittivity and increasing temperature do result in increasing ion pairs and these can be significant even for NaCl at such conditions. Fisher and Levin (1995)⁵⁵ obtained very good agreement with molecular simulation data for both VLE and critical area using the full DH theory + Bjerrum + ion-dipole terms. Just one of the two extra terms is not enough (only the latter is good for VLE and only Bjerrum is good just for critical area). For good agreement with molecular simulation, both ion-solvent interactions and Bjerrum/ion pairs should be included.

In conclusion, molecular simulation studies may provide some input towards development of e-EoS, importance of the various terms, etc., e.g. on the role of polarizability, however it appears that this may take quite some time before we have some real conclusions.

What can we learn from single-ion activity coefficients?

A tool which may be proved useful in understanding electrolyte solutions are the rather recently presented (and already much debated) “single ion activity coefficients” presented by prof. Juan Vera and his group. While these measurements have been known for some time, they have found more use only recently. Single ion activity coefficient measurements were known for years and even criticized in standard literature³ as something not reliable or based on vague assumptions. New life has been given in these measurements by the group of professor Vera and co-workers^{15,16} and numerous such data are available today. They could be used for model development and validation, something which has not been done so far for EoS. However, in two recent articles from Fraenkel (2012)⁹⁸ and Liu and Eisenberg (2015)⁹⁹, they explore the use of two different improved electrolyte models (Debye-Hückel-SiS and Poisson-Fermi) and compare the results with experimental data for single-ion activity coefficients from Prof. Vera with good results.

How should we benchmark new models?

The LLSE of water-alcohol-salts is an extremely tough test for any electrolyte model, as unlike for VLE, the electrolyte is present in both fluid phases. Very few studies with e-EoS have been reported, as mentioned above, and the results are not very satisfactory. The recently developed e-CPA EoS by Maribo-Mogensen et al., 2015⁴⁶, using salt-specific parameters performs very well over a wide range of systems and conditions (including activity coefficients extensive temperature ranges, mixed solvent systems, gas hydrates with salt+chemicals, gas solubilities in aqueous salt solutions) and in the form presented by Schlaikjer et al. (2017)⁵⁰ also for salt solubilities for a wide range of systems.

Unfortunately, the results are not satisfactory for water-alcohol-salt LLE, as shown in figure 8. The NaCl-propanol interaction parameter is either determined from solubility or directly correlated from the ternary data. The model correctly predicts a NaCl induced LLE split between water-1-propanol. However, it is clear that the driving force for ions towards the propanol phase is too weak and this may be due to the neglect of ion-ion association (ion pairs). The neutral ion pairs will be more important in the lower static permittivity propanol phase. We expect that such ion pairs will increase the solubility of NaCl in the least polar (propanol) phase.

Finally, as can be seen in figure 9, the distribution of chemicals in the two- and three-phase equilibrium is qualitatively predicted by e-CPA. The solubility of propanol in the octane-rich phase is not predicted very well if the interaction parameter $k_{ij}=0.03$ based on binary VLE is used. If k_{ij} is adjusted a bit ($=-0.0065$) rather good agreement with all phases can be obtained. There are some positive signs as e-CPA can catch both three-liquid equilibrium but also the range of salt concentrations where three phases exist. These results show that much work is needed prior to obtaining satisfactory and consistent description of this complex phase equilibria containing electrolytes. It has to be emphasized that these are very difficult systems and we have not seen many similar calculations by other electrolyte EoS in the literature.

The performance of e-CPA is much better for VLE of aqueous electrolyte mixed solvents (water-alcohol), as seen for a typical example in figure 10 for water-methanol-LiCl.

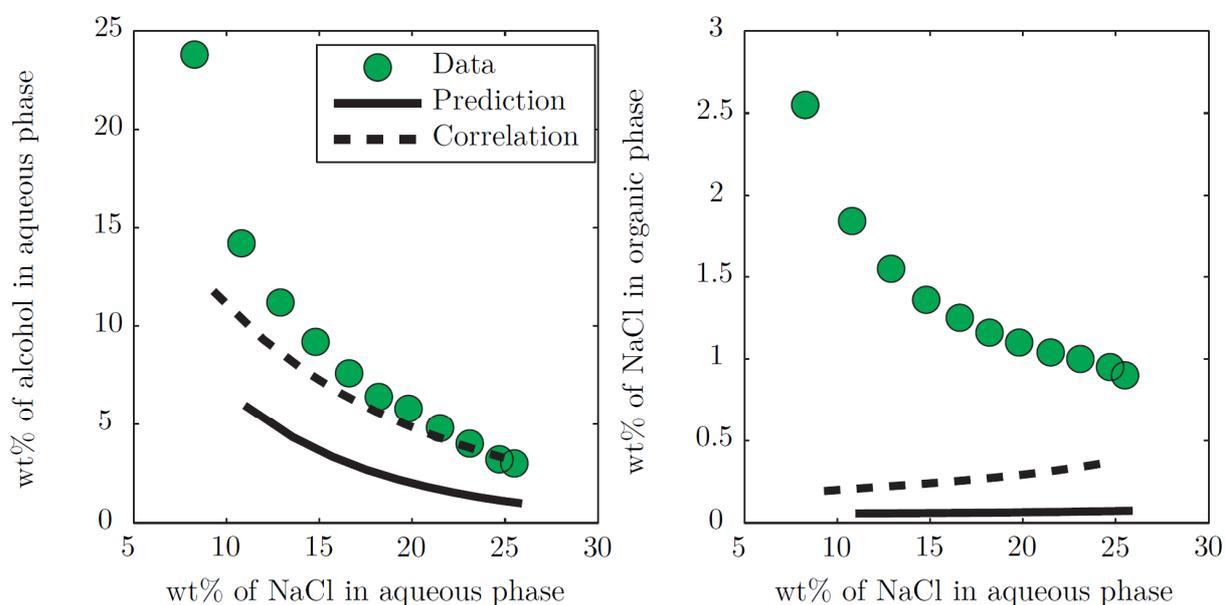


Figure 8. Distribution of NaCl and propanol in LLE at 25 °C. From Maribo-Mogensen¹². Data from ref 105.

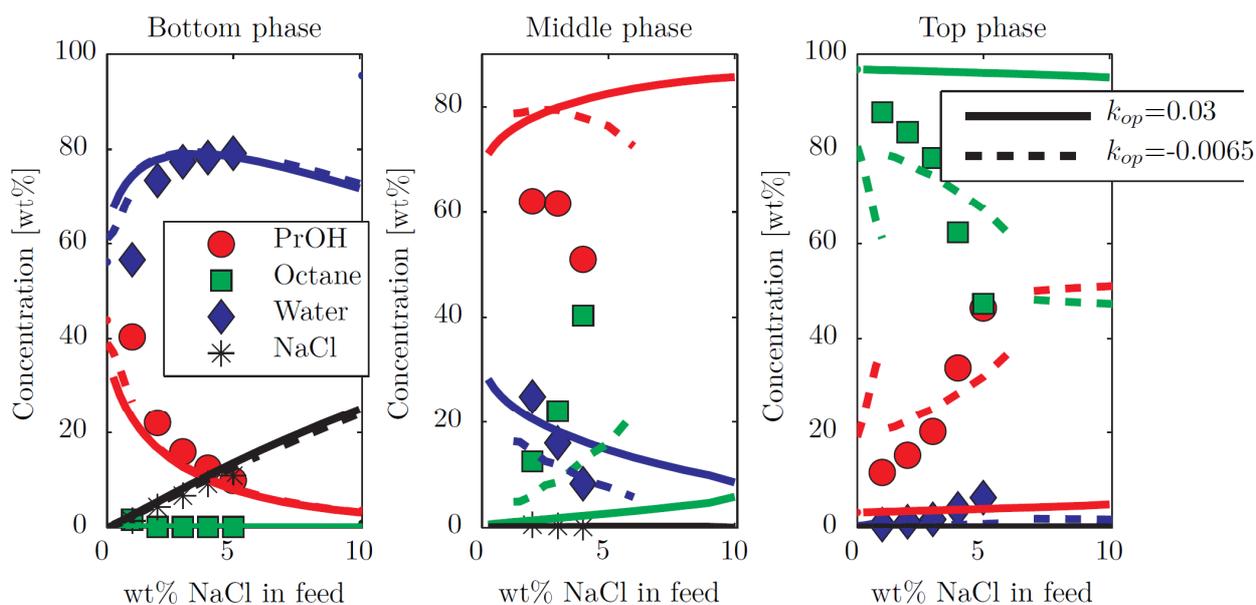


Figure 9. Distribution in three-phase liquid equilibria for NaCl-propanol-water-octane to the calculated solubility limit of NaCl (about 10.5 wt%). From Maribo-Mogensen¹². Data from ref. 106.

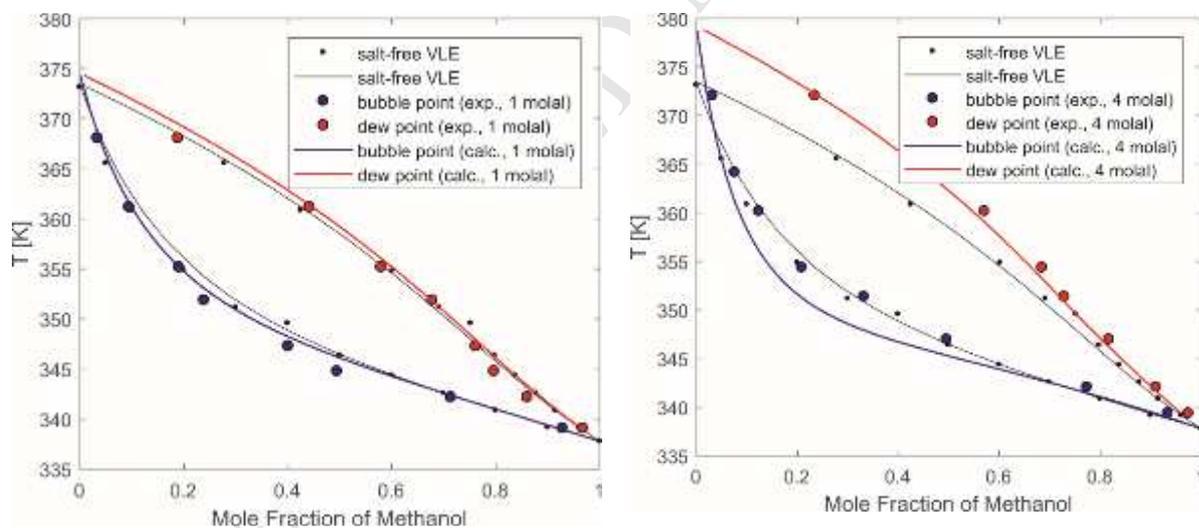


Figure 10. VLE of water and methanol in presence of LiCl at different concentrations, left: 1 molal, right: 4 molal at 1 bar. From Mark Bulow MSc thesis (2017). Data from ref 107.

1.5 The important scientific questions

From this review it is evident that the field has not yet agreed on a single approach – indeed a very wide and differently developed e-EoS have been proposed during the last 20 years or so. The large number of models is not necessarily a problem, but we fear that, unfortunately, essentially none of the following essential questions have been addressed in a satisfactory matter and in some cases some of the developments created more confusions rather than answers to the problems.

- What model should use for electrostatic interactions?
 - The primitive Debye-Hückel or MSA models or non-primitive MSA?
- Should the Born model be included?
- Do we need an ion-solvent association term?
- For primitive models: how can we model the static permittivity?
- Last, but not least, how do we estimate the model parameters in a way that makes sense and can render the model suitable for a wide range of practical applications – and if possible in a predictive way?

In a previous work, we have tried to address the point of Debye-Hückel vs. MSA and showed that the two models are in fact very similar (Maribo-Mogensen et al., 2012)⁵⁶, meaning that results should essentially be transferrable between the two. Thus, in the following sections, we will mainly focus on the Debye-Hückel model, but any point will also be valid for the (unrestricted) MSA model.

We have also addressed the point of the role of the static permittivity^{12,46-48,56} and have shown that the model chosen has a remarkable impact on the properties of the EoS (e.g. pressure and chemical potential). In fact, using a more realistic model made the EoS behave similar to the non-primitive MSA model¹², giving realistic effects on the chemical potential e.g. adding additional neutral molecules that either increase or decrease the static permittivity.

However, we still feel that many researchers are in doubt about using the Debye-Hückel model, and also unsure on whether to include the Born term. This confusion has its origins in many textbooks and publications, that cite the Debye-Hückel model as being limited to low concentrations. In order to address this confusion, we will discuss the origin and derivation of the Debye-Hückel theory with emphasis on its assumptions in the next section. We will also show how the Born term can be included in the derivation of the Debye-Hückel model.

2. The electrostatic origins of the Debye-Hückel model

The Debye-Hückel theory has been a cornerstone in the treatment of electrolyte solutions, as prior to that there was much confusion on what was really happening and how such solutions could be described. It is built on the foundations of earlier theories such as the Gouy-Chapman theory of a diffuse double-layer near an electrode interface, and was used to derive theoretical activity coefficient.

The Debye-Hückel (DH) model is one of the most widely used (and sometimes misused) approaches in electrolyte thermodynamics. An excellent starting point for understanding the Debye-Hückel model is the original article by the authors (Debye and Hückel, 1923⁴), which we recommend despite being almost 100 years old and also being written in German (which may pose difficulties to some). Still, the original article should be consulted as, unfortunately, not all followers paid sufficient attention to it. Detailed derivations and discussions are presented also in the recent literature e.g. McQuarrie (2000)⁵⁷, Sandler (2011)⁵⁸, Breil (2001)⁵⁹, Maribo-Mogensen et al. (2012)⁵⁶ and Michelsen and Mollerup (2007)⁵.

In 1975, Blum⁶⁰ derived a statistical mechanical model for electrolytes, which is often used as an alternative to the Debye-Hückel model. Figure 6 (left) shows a 2-dimensional section of an idealized electrolyte solution according to the Debye-Hückel and MSA theories. The ions are shown as spheres with unit electrical charge – in the case of MSA, the spheres are treated as hard spheres, whereas in Debye-Hückel the derivation states that there is a minimum distance of approach, and other ions cannot get any closer than this distance. The solvent (background) is shown as a uniform medium, without structure. On average, each ion is surrounded more closely by ions of opposite charge than by ions of like charge.

In the following section we will outline the derivation mainly following the procedure by McQuarrie (2000)⁵⁷, and Michelsen and Mollerup (2007)⁵. After the derivation, we will discuss the various assumptions, which may have influence on its application range, especially for concentrated solutions.

2.1. Derivation of the Debye-Hückel and Born Models

The starting point is the Poisson equation which relates the scalar electric potential field ψ_i of an ion i with the local charge density $c_i(r)$ and which, in spherical coordinates, can be written as:

$$\nabla^2 \psi_i = -\frac{c_i(r)}{\epsilon_0 \epsilon_r} \quad (1)$$

where ϵ_r is the relative static permittivity (or static permittivity) and ϵ_0 is the vacuum permittivity, and r the distance between the two charges. The charge distribution is subject to the bulk electroneutrality condition given by equation (2) and the charge of each molecule q_i :

$$\sum_i \rho_i q_i = 0 \quad (2)$$

The local charge density of the ions depends primarily on the pair correlation (or radial distribution) function $g_{ij}(r)$ through equation (3):

$$c_j(r) = N_A e \sum_i z_i \rho_i g_{ij}(r) \quad (3)$$

where N_A is the Avogadro number. The radial distribution function is related to the potential of mean force between i and j , $\omega_{ij}^{(2)}(r)$, through Eq. (4):

$$g_{ij}(r) = \exp\left[-\frac{\omega_{ij}^{(2)}(r)}{k_B T}\right] \quad (4)$$

where k_B is the Boltzmann factor. By inserting equation (4) in (3) and (1) one obtains the exact Poisson equation:

$$\nabla^2 \psi_i = -\frac{N_A}{\epsilon_0 \epsilon_r} \sum_j q_j \rho_j \exp\left[-\frac{\omega_{ji}^{(2)}(r)}{k_B T}\right] \quad (5)$$

Subsequently, the potential of mean force is estimated from the electrostatic long-range interaction energy between a charge with an electric field:

$$\omega_{ji}(r) \approx q_j \psi_i(r) \quad (6)$$

Equation (7) is inserted into (6) forming the non-linear Poisson-Boltzmann equation:

$$\nabla^2 \psi_i = -\frac{N_A}{\epsilon_0 \epsilon_r} \sum_j q_j \rho_j \exp\left[-\frac{q_j \psi_i(r)}{k_B T}\right] \quad (7)$$

Equation (7) can only be solved numerically in the general case and this use finds applications in e.g. biophysics⁶¹. To continue the derivation of the Debye-Hückel equation, equation (7) is linearized, and using the electroneutrality condition from (2) one arrives at:

$$\nabla^2 \psi_i = \kappa^2 \psi_i(r) \quad (8)$$

where the so-called Debye length κ^{-1} is defined as:

$$\kappa^2 = \frac{1}{k_B T} \frac{N_A}{\epsilon_r \epsilon_0} \sum_i \rho_i q_i^2 \quad (9)$$

The inverse Debye screening length κ , is a key property in the DH theory and it can be alternatively expressed using $F = eN_A$ (Faraday's constant). The general solution to the differential equation given by equation (8) is:

$$\psi_i(r) = C_1 \frac{e^{-\kappa r}}{r} + C_2 \frac{e^{+\kappa r}}{r} \quad (10)$$

Since the electrostatic potential vanishes with distance, it follows that $C_2 = 0$. The second integration constant is obtained by assuming that the electrical field inside the sphere with radius l_i only depends on the charge within the sphere. By equating $\left(\frac{d\psi}{dr}\right)$ inside and outside of the sphere at r_i , one can determine C_1 as shown in figure 11. Debye and Hückel only considered domain 1 and 2 in their derivation, considering the ions as point charges. However, the derivation also allows for a more general view of the ions as being spheres with surface charges, as this gives rise to the same electrical field in domain 1.

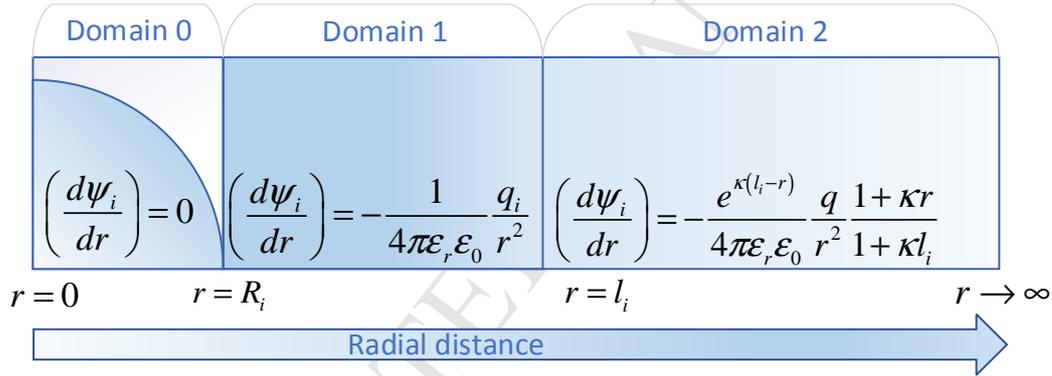


Figure 11: Three domains for the electrostatic field from an ion.

Once we have an expression for the radial-dependence of the scalar electric potential field $\psi_i(r)$, it becomes possible to calculate the electric potential of the ion using a piecewise integral from $r = 0$ to ∞ covering the three domains shown in figure 11:

$$\begin{aligned} \Delta V_i^{el} &= -\int_C \nabla \psi_i(\mathbf{r}) d\mathbf{r} \\ &= \psi_i^{(0)} \Big|_0^{R_i} + \psi_i^{(1)} \Big|_{R_i}^{l_i} + \psi_i^{(2)} \Big|_{l_i}^{\infty} \\ &= \underbrace{\frac{q_i}{4\pi\epsilon_r\epsilon_0} \frac{1}{R_i}}_{\text{Self-potential}} - \underbrace{\frac{q_i}{4\pi\epsilon_r\epsilon_0} \frac{\kappa}{1+\kappa l_i}}_{\text{Interaction potential}} \end{aligned} \quad (11)$$

Different approaches have been proposed for obtaining the electrostatic Helmholtz energy from the electrostatic approach. Originally, Debye and Hückel⁴ derived the energy from integration of the internal electrostatic energy U_{el} using equation (12):

$$\frac{A^{el}}{T} = -\int \frac{U_{el}}{T^2} dT = \int U_{el} dT^{-1} \quad (12)$$

The internal energy can be calculated from equation (13):

$$U_{el} = \frac{1}{2} N_A \sum_i n_i q_i \Delta V_i^{el} \quad (13)$$

In “modern approaches” the Helmholtz energy is derived using the partial charging process, where all ions are charged from 0 to q_i (see for details McQuarrie⁵⁷, Sandler⁵⁸ or Michelsen and Mollerup⁵). In practice this is done by replacing all charges in (13) and (11) by λq_i and integrating from $\lambda = 0$ to 1:

$$A^{elec} = N_A \sum_i n_i q_i \int_0^1 \Delta V_i^{el}(\lambda) d\lambda \quad (14)$$

By careful integration it is evident that we can arrive at the final result shown in (15) either by using equation (11) + (14) or equations (11-13), assuming that the static permittivity is independent of temperature and partial charge:

$$A^{el} = \underbrace{\frac{N_A}{8\pi\epsilon_0\epsilon_r} \sum_i \frac{n_i q_i^2}{R_i}}_{\text{Self-energy}} - \underbrace{\frac{N_A}{4\pi\epsilon_0\epsilon_r} \sum_i \frac{n_i q_i^2}{3} \kappa \chi_i}_{\text{Interaction energy}} \quad (15)$$

Where χ_i is given by equation 16:

$$\chi_i = \frac{3}{(\kappa l_i)^3} \left[\ln(1 + \kappa l_i) - \kappa l_i + \frac{1}{2} (\kappa l_i)^2 \right] \quad (16)$$

If we ignore the self-potential in equation (15), we arrive at the original expression from Debye and Hückel, which only contains the second term of equation (15).

Ideally, of course for an EoS there is no problem, as the Helmholtz energy can be first calculated (using eq. 15) with additional terms for physical effects and then the activity coefficient can be calculated from well-established thermodynamic relationships. However, in order to arrive at an expression for the activity coefficients, we must first obtain a general electrostatic Gibbs energy equation (see Breil, 2001⁵⁹) and an expression for the electrostatic chemical potential or activity coefficient. This requires us to assume that the pressure-volume work is negligible:

$$\Delta G^E = \Delta A^{el} + \cancel{\Delta(PV)} \quad (17)$$

The actual derivation of activity coefficients and excess Gibbs properties from the “electrostatic” contributions is in itself an assumption, as it requires the pressure-volume work to be negligible. Still, maybe the error from this assumption is small. Once this has been done, it becomes possible to derive an expression for the activity coefficients using equation (15), where γ^* indicates the unsymmetrical activity coefficient and γ^∞ the activity coefficient at infinite dilution:

$$\frac{\mu_i^E}{RT} = \left(\frac{\partial}{\partial n_i} \frac{\Delta G^E}{RT} \right) = \ln \gamma_i = \ln \gamma_i^* + \ln \gamma_i^\infty \quad (18)$$

In the derivation of the Debye-Hückel activity coefficients, we only consider the interaction energy from equation (15). While it is in principle possible to differentiate eq. (15) with respect to the mole numbers using eq. (18), this is not the general approach. Instead, to obtain simpler derivatives, one rewrites the Debye screening parameter (eq. 19) in terms of the molal ionic strength with respect to the pure solvent s shown in eq. (20):

$$\kappa_m^2 = B_s^2 I_m \quad (19)$$

$$I_m = \frac{1}{2} \sum_i m_i z_i^2 \quad (20)$$

Where the Debye-Hückel B parameter for the solvent s is given as (21):

$$B_s = \left(\frac{2e^2 N_A M_s}{k_B T v_s \epsilon_s \epsilon_0} \right)^{\frac{1}{2}} \quad (21)$$

Where v_s is the molar volume and ϵ_s the static permittivity of the pure solvent. Assuming that all diameters are equal, it becomes possible to derive eq. (22), which is the extended Debye-Hückel law. Note that it is also possible to derive an expression that does not assume equal diameters, see e.g. Breil (2001)⁵⁹.

$$\ln \gamma_i^{el} = -z_i^2 \frac{A_{DH} \sqrt{I_m}}{1 + Bl \sqrt{I_m}} \quad (22)$$

Where the Debye-Hückel A_{DH} parameter is given by eq. (23), which has a value of $1.172 \left(\frac{\text{kg}}{\text{mol}} \right)^{\frac{1}{2}}$ in water at 25°C, but otherwise it depends on temperature and pressure:

$$A_{DH} = \left(\frac{2\pi N_A M_w}{v_w} \right)^{\frac{1}{2}} \left(\frac{e^2}{4\pi \epsilon_r \epsilon_0 k_B T} \right)^{\frac{3}{2}} \quad (23)$$

Often Bl is treated as a constant value, e.g. $1.5 \left(\frac{\text{kg}}{\text{mol}} \right)^{\frac{1}{2}}$ (see e.g. Thomsen (2006)¹⁷), and this forms the Debye-Hückel extended law. In the limit of zero ionic strength, we obtain the limiting law from eq. (22) as shown in eq.(24):

$$\ln \gamma_i^{el} = -z_i^2 A_{DH} \sqrt{I_m} \quad (24)$$

At this point, we find it important to demonstrate that at zero ionic strength, equation (15) becomes equal to the self-potential, which is related to the Born⁶² energy of solvation of an ion from vacuum ($\epsilon_r = 1$) to a medium of an arbitrary static permittivity ϵ_r as seen in eq. (25), when assuming the pressure-volume work to be negligible (eq. (17)):

$$\begin{aligned} \Delta \mu_i^{Born} &= -\lim_{\kappa \rightarrow 0} \left[\left(\frac{\partial G^{el}}{\partial n_i} \right)_{T,P,\epsilon=1} - \left(\frac{\partial G^{el}}{\partial n_i} \right)_{T,V,\epsilon_r} \right] \\ &= -\frac{N_A}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_r} \right) \frac{q_i^2}{R_i} \end{aligned} \quad (25)$$

Note that if the static permittivity is negligible, the Born term does not provide a contribution to the unsymmetrical activity coefficients since $\ln \gamma_i - \ln \gamma_i^\infty = 0$.

The result shown in eq. (15) is final and the most general of the expressions shown. It is remarkable, as it can serve as the basis for the derivation of the extended Debye-Hückel law (eq. 22) and the Debye-Hückel limiting law in (eq. 24) as well as the Born term for ion solvation in (eq. 25).

2.2 Discussion of the assumptions and limits of application

In this section we will discuss the assumptions that went into the derivation of equation (15) and how they relate to the applicability ranges. Essentially, the assumptions begin after equation (5):

Equation (6): Radial distribution is only determined by long-range interactions

The potential of mean force between i and j separated at distance r in principle depends on the canonical average over configurations of all other (n-2) molecules⁶³, but in this step it is assumed to be equal to the long-range electrical potential between the two ions.

In the MSA model^{60,64}, a hard-sphere repulsive force was included in the derivation, and this leads to some differences in the final expression for the energy. However, a direct comparison of the full Debye-Hückel model (excluding the self-potential) given by equation (15) with the full non-restricted MSA-model showed that there are negligible differences between the two models in terms of energy and chemical potentials⁵⁶. By using a different distance of closest approach (l_i) it was possible to match the energy from MSA even up to high concentrations (5 mol/kg). A larger difference was observed in the Debye screening length (equation 9) and the equivalent Γ -parameter in MSA, which could be somewhat accounted for by including a hard-core contribution the Debye-length $\kappa^{-1} + \sigma \approx \Gamma^{-1}$.

Blum⁶⁴ also showed through comparison that the hypernetted chain (HNC) approximation using a hard-core potential at infinite dilution would give a radial distribution function approximately equal to $g_{ij} \approx \exp\left(-\frac{q_i\psi_j}{k_B T}\right)$ and thus in correspondence with eq. (8).

It should also be noted that this step in the derivation of the Debye-Hückel model from the Poisson-Boltzmann model follows the same procedure as the Gouy-Chapman theory, which finds widespread applications for the treatment of the electrostatic forces between colloidal systems and in the DLVO theory. The Gouy-Chapman theory is also based on the solution of the Poisson-Boltzmann equation and was presented in 1910 i.e. about a decade before the Debye-Hückel theory. The result of the Gouy-Chapman theory for spherical co-ordinates is similar to that from the Debye-Hückel theory, and provides the potential as a function of the distance of the surface that is calculated.

Solutions of the Poisson-Boltzmann equation, resulting to expressions for the electrostatic forces and potential, have been presented for various “geometries” for which analytical solutions are possible, even for high potentials e.g. between charged spherical particles, planar surfaces or surface-particle interactions, (see Israelachvili⁵¹ and Hunter⁶⁵ for a list of useful expressions). There have been both molecular simulation studies and experimental data for the colloid forces of various systems and there is excellent agreement with the Gouy-Chapman theory (Pashley and Karaman, 2004⁶⁶; Israelachvili, 1985⁵¹), an agreement that has astonished some researchers. Still, the Gouy-Chapman theory (as the DH theory) can be expected to have some problems for multivalent ions.

In conclusion, it appears that this assumption is not too problematic, at least at large separations or dilute mixtures.

Equation (8): Linearization of radial distribution function is reasonable

The linearization of the non-linear Poisson-Boltzmann equation (7) forming equation (8) is presumably the most important assumption in the derivation of equation (15). Without this, we cannot obtain an analytical expression. This linearization is correct when the radial distribution function can be approximated as:

$$g_{ij}(r) = \exp\left(-\frac{q_i\psi_j(r)}{k_B T}\right) \approx 1 - \frac{q_i\psi_j(r)}{k_B T} \quad (26)$$

This is a reasonable assumption as long as $|z_i e \psi_j| \ll k_B T$, an assumption which is valid in many cases. Through this inequality, we may derive the Bjerrum length, which is given by equation (27):

$$l_B = \frac{e^2}{4\pi\epsilon_r\epsilon_0 k_B T} \quad (27)$$

Bjerrum (1926)⁸³ justified the use of the linearized Poisson-Boltzmann equation even at high concentrations but he suggested to handle ions which are in close contact, a distance lower than l_B , as ion pairs, typically separated by solvent molecules but within a distance where the approximation done in equation (26) is no longer valid.

Through this concept Bjerrum improved the Debye-Hückel solution by introducing the "ion pair" through a mass-action law. There exist several analytical expressions for predicting the equilibrium constants as a function of the Bjerrum length (27), including that from Bjerrum⁸³ or the improved expression from Ebeling and Grigo⁶⁷.

Breil (2001)⁵⁹ indicates that the effect of this assumption is small for radial coordinates but there has not been any systematic comparative analysis of the full solution of the Debye-Hückel with and without the linearization assumption.

Many authors e.g. Hunter⁶⁵ state that this assumption, equation (26), often called Debye-Hückel approximation is very accurate for electrolyte solutions (but less accurate e.g. for charged colloid systems if the potential is above 25 mV).

Others have tried improving on eq. (8) by accounting for dielectric saturation effects near the ion, e.g. Liu and Eisenberg⁹⁹, but these will not be further investigated here as they require numerical solution and have until now not been used in the context of EoS. Note that if a robust solver is available, this may provide be a future alternative improvement to the Debye-Hückel equation.

It can be readily shown that the linearization assumption is more correct for symmetrical electrolytes and we should thus expect that the Debye-Hückel equation will work better for those compared to the unsymmetrical ones. This is in agreement with previous statements by Onsager, 1964⁶⁸ (Nobel Prize, 1968) who also proposed corrections of the Poisson-Boltzmann equation for unsymmetrical electrolytes. Onsager (1933)⁶⁹ showed that if higher order expansions were used instead of eq. (26) it would not satisfy the logical requirement that $\rho_i g_{ij}(r) = \rho_j g_{ji}(r)$. The Onsager criticism may indeed be valid, but he also noted that the linearized form in equation (26) does not suffer from this problem.

The linearization of eq. (8) is an important assumption in the derivation of the DH equation but, as mentioned, is an assumption which should be considered to be rather realistic and should not limit all that much the applicability of the DH equation. We find, thus, rather surprising that a number of authors limit the applicability of the DH equation to very dilute solutions, either by super-emphasizing this assumption and/or by reporting only the DH limiting law, which we will present later.

For example, McQuarie⁵⁷ uses exactly this linearization assumption for stating that it is –and thus also the DH model- valid only at concentrations less than 0.01 mol/L. McQuarie⁵⁷ presents in his derivation the comprehensive "full" solution of the DH equation (eq. 15) but he does not believe in

it! He writes “The above expressions, although frequently seen in literature, are somewhat misleading since the entire theory should be valid only in the limit of very low concentrations”.

He states that it is not correct to use the full DH equation because, due to the linearization above, the model should only be used in the form of the so-called limiting DH law (see also eq. 24).

McQuarie⁵⁷ moreover states:

“The DH theory is an exact limiting law, and we expect that the theory correctly describes the thermodynamic properties of all solutions of strong electrolytes as the concentrations approach zero. It (DH) is a reliable theory for 1-1 electrolytes for concentrations around 0.005 mol/L or less or, in other words, for quite dilute solutions.”

McQuarie⁵⁷ considers all other forms of the DH equation, even the extended DH law (eq. 22) as “strictly speaking not valid”, only useful for treatment of experimental data. Moreover, he believes that his analysis is important as “in spite of the great success of the DH theory, when it was originally proposed its range of validity was not at all clear”.

Moreover, Sandler, 2011, writes in his book⁵⁸ on statistical thermodynamics:

“A limitation of the continuum (DH) approach is that the microscopic nature of the solvent will be important when the separation distance between ions is small. Consequently, we expect that the DH model based on a continuum solvent to be applicable to dilute solutions in which there are many solvent molecules between widely spaced charged particles, but not to concentrated electrolyte solutions”.

We fear that McQuarie⁵⁷ and Sandler⁵⁸ statements and arguments are surprising and wrong as the applicability of the DH equation is not much limited by the aforementioned linearization. Even for charged particles in colloid science where complete solutions exist for many geometries, results with or without the DH approximation (eq. 15) are not much different.

To clarify some of the confusion regarding the applicability of the Debye-Hückel equation, we may use equation (27) to estimate when the linearization assumption in the Debye-Hückel model becomes invalid for a 1:1 salt, and when we may have to start accounting for ion pairs. In water at room temperature ($\epsilon_r = 78$), $l_B \approx 7\text{Å}$, which corresponds to a separation of 2 ions by a water molecule. In an ideal gas, we may approximate calculate the average distance between molecules using the Wigner-Seitz distance $a = 2\left(\frac{4\pi N_A \rho}{3}\right)^{-\frac{1}{3}}$. By equating the Wigner-Seitz distance with a scaled version of Eq. (27) we obtain that the total ion concentration where the average separation becomes equal to the Bjerrum length times a scaling parameter β (i.e. $a = \beta l_B$) is equal to eq.(28):

$$\rho_+ + \rho_- = \frac{6}{\pi N_A \beta^3 l_B^3} \quad (28)$$

Equation (28) shows that a Bjerrum distance of 7Å corresponds to approximately 4.5 mol/L of a 1:1 salt assuming an equal distribution of ions if $\beta = 1$, and approximately 4.5 mmol/L if $\beta = 10$. Naturally, some anions and cations will be somewhat closer due to the radial distribution function

(4), but if we evaluate equation (26) at the stated conditions we see that $g_{ij} \approx 4.5$ at the surface of the ion $r = l_i$ and drops to around 1 at $r = 3l_i$, giving an average value of g_{ij} from l_i to l_B of 1.5.

While there will clearly be some ion pairs at this concentration, eq. (28) serves as an estimate of an upper bound on the concentration where it is safe to apply the linearization without accounting for ion pairs. If we use equation (28), we can calculate an approximate breakdown concentration as a function of the static permittivity, as seen in figure 12 using $\beta = 1$.

Figure 12 shows that the Bjerrum length increases rapidly as the static permittivity drops, and furthermore that the concentration where the Bjerrum length equals the average distance leads to a drop in the concentration where one should be careful when applying the Debye-Hückel model. In fact, this drop in concentration could be even steeper, since the average value of the radial distribution function increases rapidly at lower static permittivities. Recall that the static permittivity decreases with the ionic strength (see also figure 13), and so e.g. in water the static permittivity at 25°C would be lower than 80.

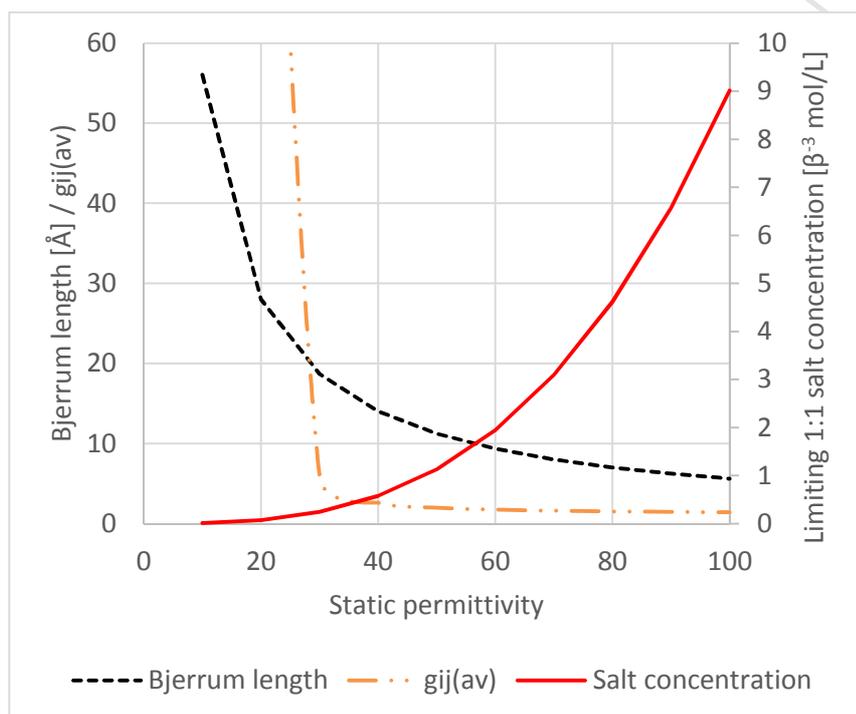


Figure 12: The relationship between Bjerrum length and limiting concentration where the average ion is closer than the Bjerrum distance, assuming $g_{ij}=1$. If the scaling factor β is 10, the right axis will be in mmol/L instead of mol/L.

It is important to note that even when the ions are within the Bjerrum distance, they are not electrostatically “neutral”. Ion pairs are instead associated with large dipole moments, and their electrostatic energy must also be counted. Originally, Kirkwood¹⁰³ derived such an equation for

molecules with large dipole moments (33.6 Debye with molecules for two ± 1 charges separated by 7Å), and more recently Fisher and Levin⁵⁵ investigated the behavior of ionic mixtures using the Debye-Hückel model with Bjerrum association and a term for the electrostatic energy of ion pairs. While the Helmholtz energy contribution for dipoles is smaller than that of ions, it is in the same order of magnitude when the dipole moments are large.

The key question is then; is β closer to 1 or closer to 10? In light of the effect of the dipole-ion interaction term from Kirkwood or Fisher/Levin and how the error of not including it may be partially compensated by the Debye-Hückel term, we think that it is closer to 1. In that case it appears that a safe application range of the complete Debye-Hückel model without accounting for ion pairs in water will be up to around 1-2 mol/L in water at 25°C. This observation fits well with what is seen in figure 1, where the extended Debye-Hückel activity coefficient model performs fairly well up to around 0.3 mol/L. Note that the extended Debye-Hückel model is different from equation (15) and subject to additional assumptions which may reduce the safe application range, as we will discuss later. Other effects, such as ion hydration should also be accounted for, and they may lead to an increasing trend, as seen in the Robinson/Stokes model (section 1.3, effect of ion-solvent association).

Equation (11): The behavior and origin of the scalar electric potential field $\psi_i(r)$

Most derivations of the Debye-Hückel model state that ions are point charges located at $r = 0$, and this has probably misled some authors to believe that the model was too crude to describe concentrated solutions. For instance, Paricaud et al., 2002⁷⁰ stated that the assumption of point charges in Debye-Hückel invalidates it at higher concentrations where ion-ion and ion-solvent correlations become important, adding that Debye-Hückel is only valid at infinite dilution.

Figure 11 offers a slightly modified view of the derivation of the Debye-Hückel equation than what is typically presented in literature. One principal misconception is that ions must be treated as point charges. However, as shown in figure 11, such assumption of point charges is **not** required in order to arrive at equation (15) as the electrical field outside of the sphere R is the same regardless of the assumption of point charges, hollow sphere, or even a uniform charge distribution (see e.g. reference 71). In fact, if we had treated the ions as point charges at $r = 0$, we would not have been able to perform the complete integration in equation (11), as the field diverges at $r = 0$.

Our approach resembles the derivation of the solvation free energy by Max Born⁶², who, assumed the electrical field to be zero in the center of the ion to calculate the potential energy in vacuum (and in the absence of other ions). Adopting this view allows us to unify the derivation of the Born and Debye-Hückel equations.

The electrical field within the ion (Domain 0) will in reality depend on the charge distribution and distribution of atoms and electrical charges. However, in practice, only the ion itself will ever experience interactions between the nucleus and the electrons and we will therefore treat the net

charge as being uniformly distributed on the surface of the ion (at the hard sphere radius $r = R_i$) and following Gauss' law, the electrical field in the center will be zero.

Domain 1 is outside the ion in a region where the electrical field only originates from the ion and can be understood as the region outside of the ion where there are no other charges present, and is equivalent to the distance of closest approach l_i . In this interpretation the only restriction to l_i is that it must be a distance where the electrical field is not affected by the other charges, and can thus also include e.g. hydration shells, but it does not depend on the other ions. l_i is the closest distance that any ion j may approach the central ion i , but this characteristic parameter cannot be known a priori and has to be fitted to some experimental data (or approximated in some way e.g. be assumed to be equal to some form of reported ionic diameter). The error in this assumption is likely greater in concentrated solutions, where ion pairs may form and the ions therefore can come in close contact at $r < l_i$.

Debye and Hückel (1923)⁴ state that for positive and negative ions of equal size, l_i should be expected to be of the order of magnitude of the hydrated ion diameter. They also state that these ion diameters cannot be identical to the diameters of the actual ions as they are surrounded by an attached layer of water molecules (for the translation of key parts of the Debye-Hückel article, see Michelsen and Mollerup, 2007⁵). Israelachvili (1985)⁵¹ reports hydrated radii for several ions much higher (2-6 times higher) than the bare ion radius (with the hydration number being larger for cations than for anions).

As Michelsen and Mollerup (2007)⁵ point out a common misreading of the original paper by Debye and Hückel is that the model is restricted to ions of equal distance of closest approach i.e. equal "ionic diameters". This is not true and in reality the diameter or minimum distance approach can be fitted for each ion, as it has indeed been done with some e-EoS models (e.g. the ePC-SAFT by Cameretti et al., 2005³⁶; Held et al., 2008, 2009^{37,38}). In this respect, there are similarities of the Debye-Hückel model and the non-restricted MSA, which also treats ions as having different diameters (which in MSA are considered to be charged hard spheres).

Equation (15): Integration paths taken to derive the Helmholtz free energy and the model for the static permittivity

Once we have an expression for the electrical potential, equation (11), it becomes possible to derive an expression for the Helmholtz free energy through either the internal energy from equation (12) and (13) or the partial charging procedure given in (14). The integration is carried out at constant temperature, volume and permittivity and both paths lead to equation (15), but they do have somewhat different assumptions;

- The energy path assumes a temperature-independent ϵ_r and l_i
- The partial charging path assumes ϵ_r and l_i to be independent of the partial charge

Both paths are somewhat problematic, as the static permittivity is not constant with respect to temperature, and as the ion becomes charged, the electrostatic potential felt by nearby molecules

will increase, leading to e.g. hydration of the ions, which may in turn also affect the static permittivity. However, there does not appear to be a simple way to obtain an analytical result without these somewhat unphysical assumptions.

The expression (15) is general (under the assumptions stated) and, even though it is derived under the assumption of constant permittivity, it does not necessarily mean that we should use the model with a constant permittivity value. It is well-established that the permittivity of water changes very much with the presence of ions (see e.g. figure 13) and, in principle, this effect should be considered when using equation (15) to evaluate chemical potentials.

Michelsen and Mollerup (2007)⁵ state: *“DH is derived under the assumptions that ions are dissolved in a continuous medium of constant permittivity. Actually the solvent is not a continuous medium, nor is the permittivity constant but these assumptions are unavoidable in the derivation. When we have derived the results, we can relax this constraint. When partial A^E -derivatives are calculated, we have to take into account that the permittivity depends on the solution properties. In dilute solutions the permittivity equals to the permittivity of the solvent, but it decreases for concentrated solutions ... and this has to be taken into account when we calculate the derived properties.”*

Others do not agree e.g. Wu and Prausnitz (1998)²⁷ write: *“The contribution of the electrostatic (MM) potential of the solvent is not obtained by differentiation of the static permittivity with respect to composition”*.

And others provide somewhat diverging thoughts e.g. Moorwood (2006)⁷²: *“The charging process assumes that the static permittivity of the solvent is constant, i.e. its value will be an effective value for the solvent mixture excluding the ions, an aspect of the theory disregarded in engineering models. We are unaware of a thermodynamic proof that the relative permittivity should not be differentiated when deriving fugacities or activities from the free energy. We feel that the contribution of the derivatives of RP (restricted primitive model) is small for a number of reasons”*. But they do not mention the reasons why the effect of the derivatives is small, and in ref. 56 we demonstrated that the static permittivity has a large effect.

Indirect evidence from experimental data supports the statement from Michelsen and Mollerup⁵ that the constraint on the static permittivity being constant can be relaxed. Figure 1 shows that the Debye-Hückel A-parameter clearly depends on composition, as the initial slope and concentration dependence differs between water and ethanol as a solvent. Figure 3 shows that the slope of the activity coefficient is dependent on temperature. Furthermore, since including the temperature- and pressure-dependence of the static permittivity in the Born-term can give excellent correspondence with measurements of solvation enthalpies, apparent heat capacities and volumes of electrolytes at high temperatures⁷³⁻⁷⁵, these observations provide indirect evidence that we may indeed **need** to include the temperature- and composition dependency of the constant static permittivity in eq. (15), when using it to evaluate thermodynamic properties in an electrolyte model. Additionally, if we include a non-constant static permittivity, but do not include derivatives in the energy it would

otherwise become thermodynamically inconsistent and lead to violation of the Gibbs-Duhem equation.

Including a concentration dependency in the static permittivity in a physically consistent manner may furthermore help to “correct” the primitive character of the theory^{47,48}. However, as discussed by Maribo-Mogensen et al. (2013)⁴⁸, the experimental data for static permittivities of mixtures containing electrolytes may be deceiving, as the mechanisms for reduction of static permittivity with salts is due to two phenomena (Hubbard, 1977^{76,77}).

The non-equilibrium originated kinetic depolarization often accounts for 25-75% of the decrease of static permittivity with concentration and the thermodynamically oriented ion solvation accounts for the remaining. The former gives a negative bias to measurements of the static permittivity in electrolyte solutions due to the movement of ions, and hence does not provide a “true” picture of the static permittivity unless the experimental data is recalculated. In principle, only the latter (thermodynamically-based ion solvation) should be considered in thermodynamic modelling. This leads to a less pronounced decrease of static permittivity with salt concentration than the experimentally measured value shown in figure 13. The remaining reduction of static permittivity due to formation of hydration shells around ions can be modeled using ion-solvent association, as shown by Maribo-Mogensen et al.⁴⁸ and recently also applied in the work by Shahriari and Dehghani⁴⁴. However, most studies^{23,26-29,33,78-82} that have included the effect of the reduction in the static permittivity on the activity coefficient from Debye-Hückel have used the unmodified data, thereby included an unphysically strong effect of electrolytes on the static permittivity which must be compensated by the remaining parameters.

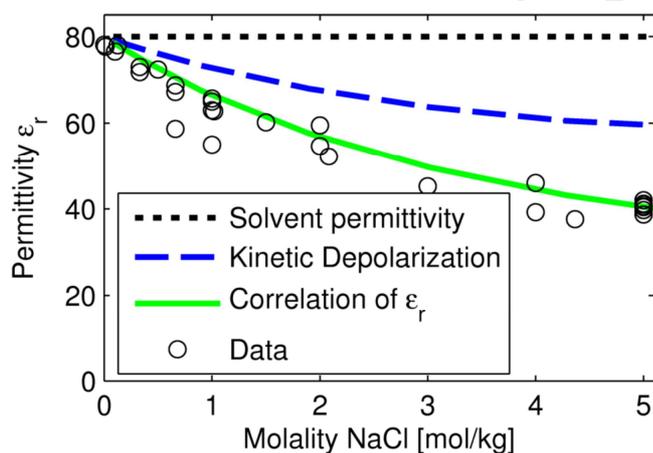


Figure 13. Reduction of static permittivity of water with NaCl. The kinetic depolarization effect is a non-equilibrium effect due to the fluctuating electrical field used in the measurement of the static permittivity. Modified from ref. 12. Experimental data from ref 100.

Equation (17): Assumption of negligible pressure-volume work to arrive at the Gibbs energy

The key assumption going from the Helmholtz free energy expression in eq. (15) to an expression for the Gibbs free energy is the assumption of no pressure-volume work. Such an assumption is not needed for an equation of state which can use equation (15) directly, but must be used in order to arrive at expressions for the activity coefficients. The assumption is likely to be reasonable at low concentrations and low pressures, but since ions exhibit quite large and negative volumes at high temperatures and pressures (see e.g. Djamali et al. (2015)⁹⁴) which can be greatly affected by the presence of other ions, it may become more problematic at high temperatures.

It is, in principle, possible to derive a general expression for the activity coefficients using Eq. (17), but this is not done in practice. Instead, the solvent is assumed to be a continuum to yield simpler analytical expressions.

Equations (19-21): Solvent as a continuum independent of mixture composition

In order to arrive at the rewritten expression of the Debye screening parameter from eq. (9) and to the solvent-specific screening parameter shown in eq. (19) one must actually make additional assumptions. The primary assumption is that the static permittivity and density only depend on the molecule that is defined as the solvent. In fact, rewriting eq. (9) in terms of the molality without additional assumptions yields eq. (9b):

$$\kappa^2 = \frac{e^2}{2k_B T} \frac{N_A x_s M_s}{v \epsilon_r \epsilon_0} I_m \quad (9b)$$

By assuming that $v \epsilon_r = x_s v_s \epsilon_s$, we may derive eq. (19). Is this a reasonable assumption in the general case? Most likely not. Often a volumetric mixing rule is used to calculate the static permittivity of a solvent (see e.g. Michelsen and Mollerup (2007)⁵), which implies that $v \epsilon_r = \sum_i x_i v_i \epsilon_i$, meaning that

in the derivation of eq. (19), we have neglected the $v_i \epsilon_i$ contribution for all other compounds. This is likely to be a good estimate only in dilute concentrations. Furthermore, the volumetric mixing rule for the static permittivity is, in itself, an approximation, and a complete treatment such as that presented in Wang and Anderko⁸⁰ or Maribo-Mogensen et al.^{47,48} should be preferred.

This means that eqs. (22-24) must be thought of as unsymmetrical activity coefficients in a single solvent, as they have not been derived assuming that the density or static permittivity is equal to that of the solvent, in this case water. Furthermore, they are only valid at low concentrations, at least lower concentrations than the complete expression shown in eq. (15).

Another problem with the formulation in terms of molality is that it requires that the solvent is present in large quantities since the molality is defined as $m_i = x_i (x_s M_s)^{-1}$. When the solvent mole fraction goes towards 0, $\kappa_m \rightarrow \infty$, which can lead to numerical errors when evaluating activity coefficients.

Equation (22): Assumption of equal distance l_i for all ions

Equation (22) can be derived from eq.(18) by assuming that all ions have the same limit l_i . This is not necessarily a reasonable assumption, as there can be large differences in the sizes between e.g. a Li^+ ion compared to tert-alkyl-ammonium ions. However, once this assumption is made, one can arrive at the simple expression for the Debye-Hückel extended law shown in eq.(22). Additionally, the value of B is often assumed to be independent of temperature and pressure, which is reasonable, as can be seen in Figure 14, once the value for l has been fixed. However, different values of l change the behavior of eq.(22), and this will affect predictions.

Equation (22) is used in many popular and highly successful electrolyte activity coefficient models like Extended UNIQUAC^{101,102}. The inherent assumption leading to eq. 22 is that the static permittivity and density are independent of the ions. However, Hückel⁸⁵ noted that if the static permittivity was assumed to depend on the ionic strength in a linear fashion, $\epsilon_r = \epsilon_w (1 - \delta I_m)$, one may obtain equation (29):

$$\ln \gamma_i^{el} = -z_i^2 \frac{A\sqrt{I}}{1 + B\sqrt{I}} + CI \quad (29)$$

where A and B are defined as in the extended Debye-Hückel equation above and C is an adjustable parameter (function of temperature and of the ions in the solution). It accounts indirectly for the composition dependency of the static permittivity and its effect on the activity coefficients.

Guggenheim (1935)⁸⁶ noted that if the C -parameter was treated as an adjustable parameter, one could obtain quite satisfactory agreement with the activity coefficients of HCl up to high concentrations. However, the value of this C -parameter was so large, that it would indicate that the static permittivity would become negative at 25°C, if the inherent linear model was used, thus the method must be considered as an empirical coefficient. Guggenheim suggested instead that the C -parameter was due to the specific interactions between species⁸⁶, the Specific Ion Interaction Theory. This expression, as discussed by many (Thomsen, 2006¹⁷; Sandler, 2011⁵⁸; Helgeson et al.⁸⁷; Prausnitz et al.³), gives excellent agreement with experimental activity coefficients up to very high concentrations. Its range is often defined as $I < 0.5$ or by others (Sandler, 2011⁵⁸) up to 16M, which is several orders of magnitude higher than both of the previous “simplified DH equations”.

A word of caution: while the Hückel expression can be used to fit data well for single salts, it is not easy to generalize to other solvents. We believe, that in order to be thermodynamically consistent, one must derive the activity coefficients using eq. (18), and so a concentration dependence cannot be introduced in eq.(22) a posteriori without the risk of being thermodynamically inconsistent. A correct procedure would be to return to the original expression eq. (15) and re-derive expressions for the activity coefficient using eq. (17) and (18) assuming a concentration-dependent static permittivity and volume, including the effect of mixed solvents and other compounds in the medium. If we use eq.(15) as starting point, but include a concentration-dependent static

permittivity and volume this will lead to different expressions than eq.(22), but should always lead to the same limiting law eq. (24), which is exact and has been measured to high accuracy.

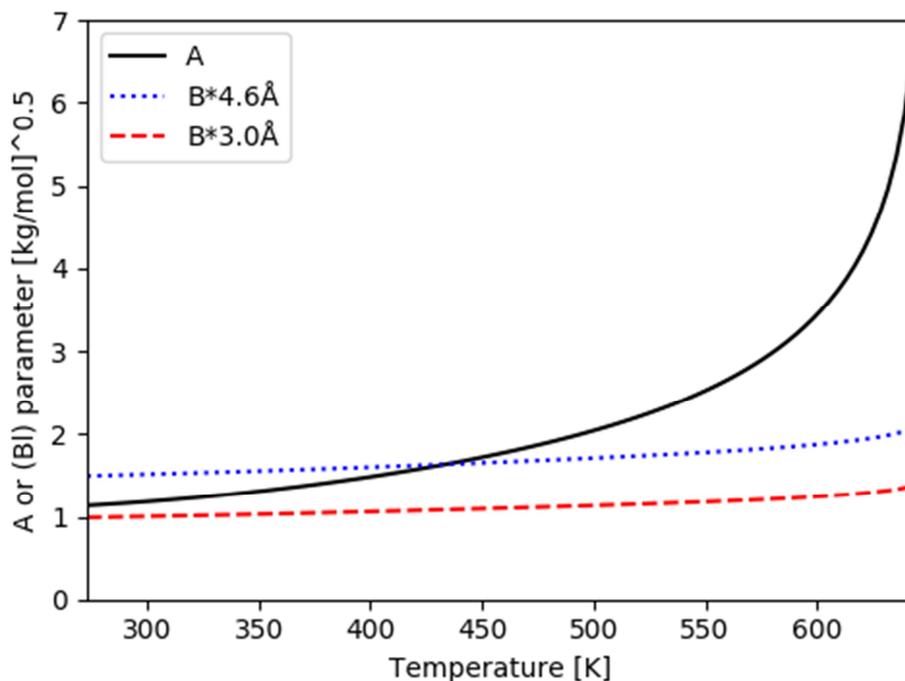


Figure 14: The value of the Debye-Hückel parameters for liquid water at the saturation point as a function of temperature.

Equation (24): The Debye-Hückel Limiting Law

Equation (24) is often called the “Debye-Hückel limiting law” and can be obtained from equation (22) by a Taylor expansion at $I_m = 0$. This is the often used form of DH mentioned in many textbooks and is only valid for extremely dilute solutions ($I < 10^{-3}$, roughly 0.01 M). This is further discussed by Thomsen (2006)¹⁷, see also figure 15, which shows how a plot of χ_i parameter dependency on salt concentration for two different values of $B l_i$. It is illustrated that this parameter is very sensitive to changes in ionic strength, even for a 1:1 salt, but also that the value of l_i can have a significant effect on the concentration dependence of the χ -function. Essentially this illustrates that eq. (24) is correct only in the limit of infinite dilution.

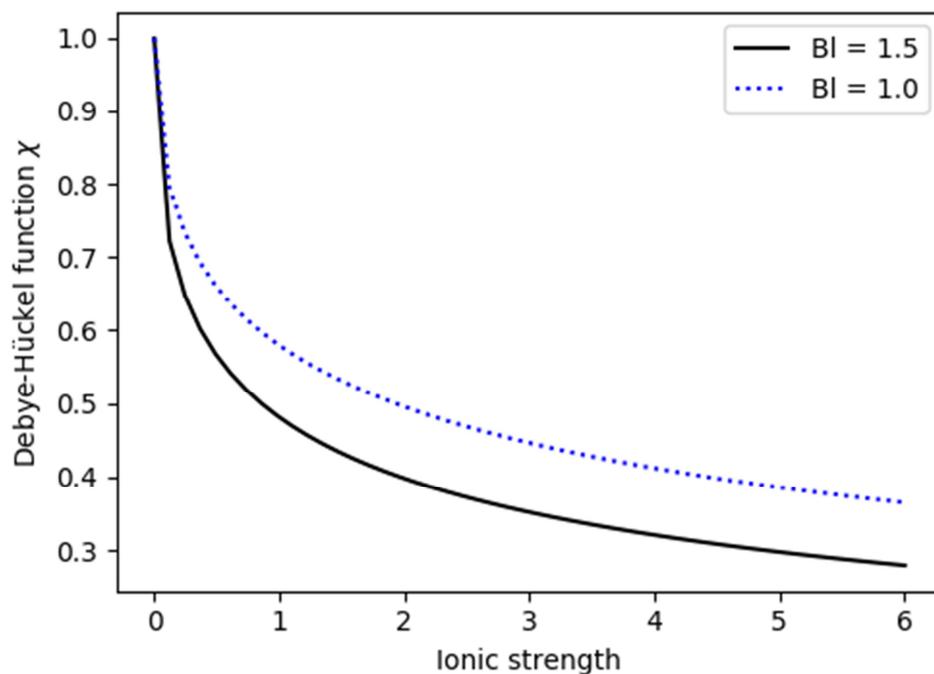


Figure 15. The chi-parameter of equation 15 (i.e. eq. 16) as a function of the ionic strength for a 1:1 salt e.g. NaCl.

In the limiting DH law is inherent the assumption that the Debye length is much higher than the ionic diameter, whereas both parameters are of the same magnitude. This is clearly a very wrong assumption at higher ionic strengths.

In well-known textbooks like Prausnitz et al., 1999³, the general solution of the DH equation, eq. 15, is not even mentioned (not even that it exists...) and only the “simplified” versions shown in equations 22 and 24 are reported. Actually, the DH limiting law, eq. 24, is presented as the major theoretical result coming out of the derivation by Debye and Hückel. This is a surprising result and from such an excellent monograph. Nevertheless, other recent books⁸⁴ do mention the general solution of the DH equation.

Some of the reasons which have led to misconceptions regarding the DH theory’s actual application range can be traced back to the many “simplified” versions of the theory which can be derived from equation (15) under certain simplifying assumptions.

- i. These simplified expressions can be derived from the general DH theory, eq. (15), but the derivations and assumptions associated are not mentioned and very often the original DH theory from where they were derived is not mentioned either!
- ii. They are often presented in the form of activity coefficient, which is an approximation and moreover moves focus from the more rigorous Helmholtz energy expressions.
- iii. They are sometimes called “laws” or “limiting laws” and are often associated with statements about the “application range” of the DH theory to “very dilute solutions”. In

reality, it is these “specialized simplifications” which are limited to dilute electrolyte solutions.

The discussions about eqs. (22) and (24) reveal some of the problems but also the capabilities of the DH approach. While we fully appreciate the practical applicability of the engineering electrolyte activity coefficient models, we think that all these assumptions cause confusion and “mask” the true value of the DH theory. None of the assumptions made in order to derive equations 22 and 24 are needed or are implied in the DH derivation, eq. 15. Thus, both equations can be considered rather extreme simplifications of the full DH equation. We consider thus surprising that equations 22 or 24 are presented in numerous textbooks, including the ones providing a “full” derivation of the DH equation e.g. Sandler⁵⁸ or McQuarie⁵⁷, as “proof” that the validity limits of the DH equation are “dilute or very dilute ionic solutions”. This is simply not true!

In reality, there is no reason for not using, at least for EoS, the general DH equations (eq. 15). While there are indeed some assumptions in the derivation of the general Debye-Hückel equation shown in (15), most physical-chemistry and thermodynamic textbooks^{3,89,104} do not mention this general model and instead present the simplified results (eqs. 22,24), which rely on much stricter assumptions and simplifications only valid at very low concentrations.

Equation (25): The Born term and its significance

This brings us to a discussion of the Born term (Born, 1920⁶²) (Nobel Prize 1954), which can be derived as shown from the first term of the above shown general DH equation (15) as shown in eq. (25). This is an old established term and is often called solvation or “ion self-energy” (self-charging energy) and corresponds to the electrostatic energy of the ion in a vacuum or in a medium even in absence of interaction with other ions. It may also be used to determine the Gibbs energy of transfer between two different medium of static permittivity ϵ_1 and ϵ_2 .

In primitive theories involving electrolytes in multiple phases it can have a great importance and in the non-primitive theories it is replaced by the ion-(induced)dipole interaction. Israelachvili⁸⁸ has shown that the Born term can be derived either from a continuum (primitive) or a molecular approach. According to Israelachvili, with his derivation, we gain additional insight into the limitations of the Born equation. He concludes that the Born equation will be widely valid for many systems except for small or multivalent ions in very polar solvents such as water.

The Gibbs free energies of hydration estimated from eq. 25 are in reasonably good agreement with experimental data (Laidler and Meiser, 1999⁸⁹; Thomsen, 2006¹⁷), indicating that the theory accounts rather well for the main effects (the smaller the radius and the higher the charge the worse the results are). According to Rashin and Honig (1985)⁴⁵ the radius value used in eq. 25 has a significant effect on the hydration energy values. Best results are obtained by using R-values 7% higher than the ionic radius (anions) or the covalent radius (cations). Myers et al.³² also state that

cavity ionic diameters that should be used in the Born equation must be higher than the (bare) ionic diameters (0.1 Å larger for anions and 0.85 Å larger for the much more hydrated cations). There is some criticism of the Born equation and it has even been recently suggested (Bashin, 2012⁹⁰) that eq. 25 should only be used for calculating the solvation enthalpy and not the free energy. We note that in the context of EoS, this is not a problem since eq. (15), does not neglect the pressure-volume contribution. Still, the results shown by Rashin and Honig (1985)⁴⁵ and others confirm that the Born theory provides an accurate means for calculating the solvation energies of ions in water.

A further discussion of the various “radii” is shown in Table 3, which compares some ionic radii from Born and from the experimental data, as reported by Marcus (1997)⁹¹. Born (1920)⁶² estimated the solvation radius R_i by setting the work required to charge the ion in vacuum equal to the ionization energy or electron affinity of a range of molecules. Note that this approach neglects change in the ideal gas entropy. The Born radius is, in all cases, higher than the Marcus (experimental) radius. The same is true also when we compare the Born radius with another source of experimental data for ionic radii (Pauling values). The differences between the measured ionic radii and the calculated Born radii is often interpreted as being due to the inclusion of the solvation shell surrounding the molecules. As mentioned, for this reason these radii are often estimated in the context of a model from experimental mixture data e.g. mean ionic activity coefficients (simultaneously with the remaining parameters).

Table 3. Ionic radii as calculated from Eq. 25 (Born radius) and measured ion. From Marcus (1997)⁹¹.

Ion	R_{Born} [Å]	R_{Marcus} [Å]	$R_{\text{Born}}/R_{\text{Marcus}}$	$R_{\text{Born}}-R_{\text{Marcus}}$ [Å]
H ⁺	0.53	-	-	-
Li ⁺	1.34	0.69	1.93	0.64
Na ⁺	1.40	1.02	1.37	0.38
K ⁺	1.65	1.38	1.20	0.28
Mg ⁺⁺	1.27	0.71	1.79	0.56
Ca ⁺⁺	1.60	1.00	1.60	0.60
F ⁻	2.11	1.33	1.59	0.78
Cl ⁻	1.99	1.81	1.10	0.18
SO ₄ ⁻	8.44	2.30	3.67	6.14
NO ₃ ⁻	1.83	1.79	1.02	0.04
OH ⁻	3.94	1.33	2.96	2.60

Finally, it is worth mentioning that the Debye-Hückel and Born expressions can both be derived from electrostatic principles as shown in section (2.1) and actually both are needed in implementations of electrolyte EoS¹². In equation (15), the Born radius and the distance of closest approach are not strictly correlated and the Born radius could be treated as an adjusted parameter fitted to the Gibbs energy of hydration data. Equation (15) is further supported by by Israelachvili's (2012) derivation of the interaction energy between ion and dipoles (first shell contributions only)⁸⁸.

3. Final words

We have set the picture, asked many questions, provided a few answers, presented the current state-of-the-art and several of the debates and left many questions unanswered. This is not an easy topic.

Question remains - how much “more physics” is needed for modelling satisfactory electrolyte solutions ? Do we need a “full” model, as shown in figure 7, i.e. with additional contributions for ion-solvent association and Bjerrum association (ion pairs) i.e. having what Robinson and Stokes called as “civilized models” ? Are ion-ion short range interactions of association or of dispersion (physical forces) nature? Or can these and potentially other missing effects be accounted for by some “intelligent” parameter estimation ?

These are difficult questions, and we have a long way to go. This can be made even clearer by considering an almost 30 years old academia-industry Panel discussion (published in FPE 1983, volume 14). John Prausnitz was then predicting that in the years to go we would see:

- Semi-theoretical EoS for complex mixtures
- Abandoning quadratic mixing rules
- EoS for petroleum fractions and for polymers
- New techniques for incorporating in EoS scaling laws for the critical region of pure fluids and mixtures
- A comprehensive framework for multicomponent mixtures containing aqueous electrolytes solutions with hydrocarbons and weak electrolytes as well (CO₂, ammonia, acetic acid)

And he also predicted a consolidation of models: *”At present,... we use the Wilson equation for mixture of water and ketone; the Redlich-Kwong EoS for a mixture of methane and CO₂; the Flory-Huggins for polymer solutions and some form for the Debye-Hückel theory for aqueous solutions of salts. I see a trend which will both extend and consolidate many of these theories and correlating equations. At present, applied thermodynamics is a tool box with very many tools, each designed for a particular job. I expect that, if current trends continue, in a few years we will have not only better tools but also fewer tools for covering a much wider range of problems”*.

This review illustrates that there are still many (maybe far too many) both fundamental and practical challenges to be addressed in the field of electrolyte thermodynamics. Maybe future research will help provide some answers.

We started this review by stating a number of questions related to electrolyte thermodynamics, with special relevance to modeling using electrolyte EoS. More questions came on the way while analyzing the Debye-Hückel and Born terms. We have provided some answers whereas several questions remained unanswered. We do not claim we have all the answers, in fact we are not sure answers are available for all of these questions. For some of these questions, only personal opinions or speculations can be provided. We have summarized in Table 4 several of the relevant questions and challenges and some answers or opinions based on our experience in the field (and study of pertinent literature).

In conclusion, we believe that future developments in electrolyte thermodynamics need to carefully consider all questions in Table 4. We possibly need more fundamental understanding and fewer electrolyte EoS whose modeling and correlative capabilities most often depend largely on the database used in parameter estimation and a large number of adjustable parameters and which are of limited, if any, predictive value.

This had been emphasized 20 years ago in their review of electrolyte models by Loehe and Donohue (1997)⁹⁵ where they wrote *“If published reports of new EoS claiming wide applicability were to provide the quality of the fits to set of standard applications, much time and effort would be saved by non-specialists attempting to use the EoS for engineering calculations. We would like to see a cessation of what has become the practice of promoting an equation’s strengths without a discussion of its limitations”*.

We completely agree and this statement is 20 years old when only a few electrolyte EoS were available. This is much more the case today where we do not think that Loehe and Donohue⁹⁵ wish has been fulfilled.

Table 4. Questions and challenges related to electrolyte thermodynamic (modelling) and some answers – the authors’ opinion.

Question / Challenge	Answer – Opinion by authors	Comment
Which is the best theory for ion-ion interactions, Debye-Hückel or MSA ?	The differences between the “full” version of the Debye-Hückel and MSA are indeed small even at high concentrations and both have been used successfully in electrolyte EoS. Debye-Hückel in its full version has been successfully combined with both SRK in the e-CPA model and with PC-SAFT. Both should work satisfactorily up to relatively high concentrations.	Use always the full version of DH, no reason to use the simplified versions of DH in EoS – these versions do come from the general equation in the limiting or other simplifying cases
Is the DH and/or MSA theories good enough for ion-ion interactions ?	We would think so. Maybe there are problems for very large and unsymmetrical electrolytes, though this is not fully documented from the practical point of view	Problems at high temperatures and very high concentrations may be due to ignoring ion-pairing terms

Do we need the Born term in modeling ?	Most recent studies point out that it is of the same magnitude as the ion-ion interactions, either from DH and MSA, thus presumably very important	Hydration free energy data can be used to obtain the Born radius.
Is the primitive or the non-primitive approach the way to go?	Hard to say – maybe in 50 years the non-primitive approach will prove to be better. For the time being, the primitive approach appears to be both sufficient and yielding rather good results	Very few groups work with the non-primitive approach and they do not appear to pursue this systematically. We will see what the future will bring.
Should the static permittivity be considered constant or should we account for the concentration dependency including all derivatives ?	Question valid for the primitive approach. Hard to tell. There are no systematic studies, but eq. (22,24) were derived assuming that it was independent of concentration, whereas this is not the case for (15). For mixed solvents, the concentration dependency appears necessary but whether this is needed for single solvent-electrolyte systems, this is unclear.	For the non-primitive approach, the static permittivity is an output.
Does it matter which physical term is used in e-EoS e.g. cubic vs SAFT and which SAFT version ?	It does not seem to be the case. There are no direct comparisons. But nothing in the current literature points towards any importance of which physical term is used.	In all models, there are adjustable parameters in both the physical and electrolyte terms – with the size (ion diameter) parameter appearing in both terms
Do we need the Bjerrum association or similar term to account for ion pairing ?	Very hard to tell. From the theoretical point of view, yes. From the practical point, it is not clear whether it is really needed esp. if Born/concentration dependent static permittivities are used. In low-permittivity solvents ion-ion association is more likely to be useful/needed.	Experimental data for electrical conductivity can be used to assess the extent of ion association.
When do the physical	At high concentrations... but	Fitting of empirical binary

interactions start becoming important /more important than the electrostatic ones ?	how high this is difficult to say. Ion-solvent association may be important even at low concentrations, since the association and short-range dipole-ion interactions are strong.	interaction parameter to experimental data makes it difficult to get insight into the true nature of the physical interaction, as they can hide and compensate for errors in the electrostatic term.
How many and which terms should we use in e-EoS ? For engineering applications ?	Hard to say – we believe an association EoS, CPA or SAFT, should be used for the physical terms and at least ion-ion and ion charging (Born) terms are needed. For ion-solvation and ion-pairing terms, whether their effect can be covered by adjustable parameters remains to be seen	The many adjustable parameters have been a curse for electrolyte modeling, as the number of pairs increase exponentially. We should strive to have a predictive theory (without adjusting interaction parameters, $k_{ij} = 0$) and only adjust parameters when needed.
Ion-specific or salt-specific interaction parameters?	Both are useful, the latter esp. during the early developments of a model, but any final models should include ion-specific parameters	Ion-specific parameters require fitting many parameters for many salts simultaneously. This may be both difficult and time consuming and there is no guarantee for optimum solutions – there may be more than one parameter set that fits all data equally well -but which will extrapolate better?
Which ion diameters should we use?	The Born radius, hard sphere diameters, etc. may not be correlated through simple expressions and should in principle be fitted. If they are fitted, one should recover correct physical trends such as increasing diameters for each period.	There are numerous sources for “ionic” diameters are available (Pauling, Stokes, Marcus, Born, hydrated,...; see also Table 3 and discussion thereof).
Which data should be used in parameter estimation for e-EoS?	At least VLE and activity coefficients (mean ionic and osmotic), preferably at various temperature and possibly also salt solubilities (SLE). Optionally, also densities	Crucial to include a variety of salts, and not just 1:1 but also heavy and non-symmetric salts as well. Equally important to use data over extensive T-ranges as using data only at room T will

	<p>which can have a large effect on the parameters and performance for the other properties.</p> <p>Finally, thermal property data can be useful. Excess enthalpy is the temperature derivative of the activity coefficients and therefore helps to give the model parameters the correct temperature dependency. Enthalpy data also help to distinguish between temperature effects and concentration effects.</p>	<p>result to biased parameters most probably and possibly poor results at higher T.</p> <p>When SLE is also considered for many salts the standard state properties will also need to be fitted.</p>
Which data should be used for testing – validating the models?	All data not used in parameter estimation, but certainly mixed salts and mixed solvents - VLE and LLE are both very important tests	
When do we know we are in trouble or (from the opposite side) we know we have developed a truly useful theory ?	Ternary and quaternary LLE data with mixed solvents and mixed salts as well as thermal and volumetric properties – if these can be represented well with parameters based on the data mentioned before, then for sure we are close towards developing a truly useful model	This is very tough ! Only less than 10% of the eEoS even briefly consider ternary LLE or thermal effects
What can be done with standard state properties for solid salts needed for SLE calculations ?	Difficult question – today for most practical purposes, they should be fitted to experimental data (SLE) simultaneously with the other model parameters, especially for the most complex and heavily hydrated salts. Few values can be “considered” experimental and with some approximation some values can be taken from other models.	This is a serious problem and possibly the reason why there are so few e-EoS showing SLE (salt solubility at various temperatures) calculations. It is uncertain whether e-EoS solely optimized on activity coefficients will be suitable for SLE calculations, as the model parameters need to be re-estimated. Such SLE calculations are typically carried out using electrolyte activity coefficient

		models. However, EoS should be able to do just as well, if the solubility constant is tuned to experimental data.
What about single activity coefficients ? Are they real ?	Hard to answer but the work of prof. Vera and co-workers surely is very convincing. Such data may be useful in model development and testing if verified by other researchers	Not verified by many researchers outside prof. Vera group. Hasn't been used in an e-EoS development so far.
McMillan – Lewis Randall frameworks. Does it matter ? Do we need conversions ?	No, we do not think it matters in an EoS. Very few have used such conversions and they do not appear to be significant, not even for mixed solvents.	They may have merit when converting data using Gibbs free energy models.

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