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A review of electrolyte equations of state with emphasis on those based on cubic and cubic-plus-association (CPA) models

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Abstract

Electrolyte thermodynamics is a complex and broad subject of immense importance in very diverse applications. The models proposed for electrolyte solutions have some similarities to those for non-electrolytes but also significant differences. Not just due to additional contributions but also because of the way the models are developed for electrolytes vs. non-electrolytes. Moreover, there are still fundamental issues unresolved in electrolyte thermodynamics.

It is still today the activity coefficient models, often extensions of local-composition models, that are used in engineering practice for electrolytes e.g. the Pitzer, electrolyte NRTL and extended UNIQUAC. In this review, however, we investigate the area of equations of state (EoS) for electrolytes, a very rich field which essentially started with the Fürst and Renon model in 1993. Since then numerous electrolyte EoS (e-EoS) have been proposed; the literature is both rich and confusing. We have decided in this work to review mostly electrolyte versions of cubic and CPA (Cubic-Plus-Association) EoS, although some of the observations made may be applicable to e-EoS of the SAFT type as well, and some of them are also briefly discussed. Reviewing e-EoS is not an easy task due to especially the diversity of modeling and parameter estimation approaches which are followed as well as the way the models have been validated. Almost none of the e-EoS proposed in literature can be compared “on equal terms” with another e-EoS. Thus, a critical comparative analysis is proposed here, including some recent developments of the e-CPA approach. When possible, different modeling - parameter estimation - validation approaches are compared. It is hoped that this review can provide an insight on the current state-of-the-art of some e-EoS proposed in literature and point out areas where further research is needed.

1. Introduction and motivation

The thermodynamics of electrolyte solutions plays a very important role in many applications in engineering (e.g. chemical, electrical, petroleum, environmental), in material science, geology but also in biotechnology, physiology and medicine. It is, thus, not surprising that a large number of electrolyte models have been developed over the years. The most well-known engineering models (e.g. those available in process and other simulators) are those based on extensions of local-composition and other activity coefficient models to electrolytes. It is especially the electrolyte versions of NRTL (e-NRTL), UNIQUAC (extended UNIQUAC), the OLI and the Pitzer models that are typically used today. These models, including references to original publications, are discussed in many reviews (Prausnitz et al. [1]; Kontogeorgis and Folas [2]; Pitzer [3]; Thomsen [4]). They have a large number of adjustable parameters, which are often fitted to a wide range of experimental data and can be typically used within the temperature and concentration conditions considered in their developments. They perform less satisfactorily for extrapolations and it is difficult to develop generalized trends for their parameters. Their theoretical foundation is also often questioned. Despite the above, they are indeed useful and we envisage that they will continue to be used for many years ahead. The industrial significance of these models is also evident in reviews presenting industrial requirements on thermodynamic properties (Hendriks et al. [5]; Kontogeorgis et al. [6]). In the same reviews is also expressed the general view that, while the classical models mentioned above are still very useful, the industry would welcome new developments in electrolyte thermodynamics leading to models having a potential broader range of application.

The purpose of this work is to review another class of thermodynamic models which have the potential of becoming useful models for engineering applications; the electrolyte equations of state (e-EoS). Over the last 40 years numerous such models have been developed, the vast majority under the so-called “primitive” approach, where the solvent is considered to be a dielectric continuum (and is not “rigorously” considered to be molecule at least with respect to the electrostatic forces). In this review we will limit our discussion mostly on e-EoS having cubic/cubic-plus-association (CPA) terms for the representation of the physical interactions (between solvents or solvents and ions), while equations of state based on SAFT, other theories and the few non-primitive approaches may be considered in a subsequent study. Still, a few remarks on e-SAFT approaches will be made.

There have been some few (relatively short) reviews of e-EoS (Kontogeorgis and Folas, 2010 [2]; Kontogeorgis et al., 2018 [7]; Galindo and McCabe, 2010 [8]; Tan et al. [9]). None of them are very detailed or attempt a comparative discussion of the various approaches. In addition, a number of publications or PhD theses have presented short comparisons of various e-EoS and their characteristics [10,19,54,57,67b]. Even in the earlier years of e-EoS development, the situation was confusing as J.R.Loehe and M.D.Donohue had stated in 1997 [AIChE J., 43(1): 180]: *“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".*

Thus, as we believe that the large number of e-EoS has caused significant confusion (not to mention stagnation in some of the developments), we have decided to follow a different approach in this review, which is presented next.

First of all, the models reviewed here are graphically presented in figure 1, illustrating that they have distinct contributions from the short-range forces (e.g cubic equations of state or SAFT), maybe additional term for hydrogen bonding interactions (e.g CPA, SAFT) and one or more additional contributions for the electrostatic contributions. All models we review have at least one additional term for ion-ion interactions (taken either from some form of the Debye-Hückel or MSA theories) and they may have more terms e.g. a Born-type term for solvation effects.

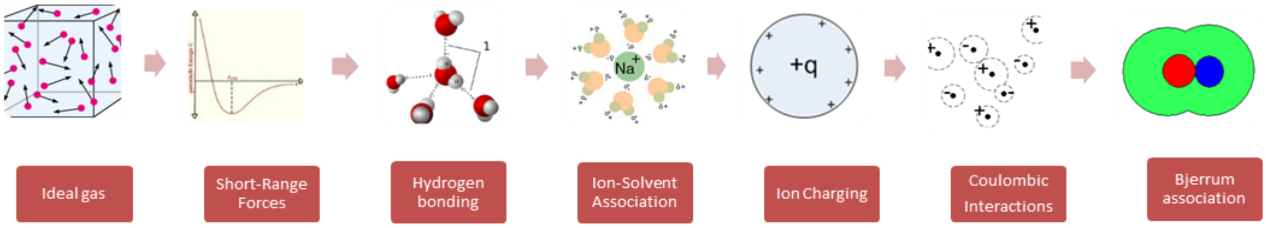


Figure 1. Contributions to (the Helmholtz energy form of) an electrolyte equation of state. In addition to contributions from physical and chemical (hydrogen bonding) forces, such models include various contributions to electrostatic (Coulombic) interactions, possibly also including effects from ion-solvent and Bjerrum associations (ion-pairing). From Maribo-Mogensen [10].

All the models we consider in this review have the general form shown in figure 1. What is implied from this is that we will not consider in detail here two other types of e-EoS based on cubic EoS; the Søreide-Whitson method [11] and the EoS/G^E approaches like PSRK/LIFAC [12] and others. The former is of semi-empirical value at best and used in diverse gas-related and petroleum applications but not beyond that. The latter is essentially the incorporation of an explicit electrolyte activity coefficient model (LIFAC in this example) inside the cubic EoS via the so-called EoS/G^E mixing rules. The success of the final model will largely depend on the incorporated G^E model.

Where this review differs, we believe, from literature is on the main objective, which is to provide a rather critical point of view, to "look behind the lines" in the proposed models (e-EoS). Thus, the purpose is to reveal what is *really* written in the original manuscripts and provide "qualified guesses" about what is *not* written and in this way attempt to conclude what we **really** learn about the proposed models. Of course the original equations for all models are provided in the references cited in this review but we will also emphasize which data are used and not used for parameter estimation and we will compare the different modeling approaches sometimes employed by the same research groups. Moreover, we will summarize the lessons obtained and the messages received which hopefully in the future can lead to a convergence of approaches and some consensus regarding where the modeling of electrolyte systems using e-EoS should go. For some models we are particularly familiar with, the e-CPA EoS, we will compare various modeling approaches so that we can conclude on the significance and differences of parameter estimation methods within the same equation of state framework, something we rarely see in literature.

More specifically, we will look at the proposed models in the following (highly inter-connected) directions:

- Can we overall compare the proposed e-EoS based on the information provided in the manuscripts and our understanding? Can we conclude on which e-EoS may overall be the most suitable one ? And more specifically which of the underlying theories (those representing physical and electrostatic interactions) are likely to be the most correct ?
- How general are the proposed models ? (an electrolyte EoS is expected to be able to provide VLE, LLE, SLE, solvation energies, thermal, volumetric properties, etc over a wide range of systems including mixed salts and mixed solvents and over a wide range of temperatures, pressures and compositions)
- How are the various models developed (i.e. how many and which parameters are fitted to experimental data and which data are used) and how are the models validated (i.e. to what extent are the results presented merely correlations, or extrapolations and when can they be considered to be predictive)
- How are the various models developed in terms of fundamentals e.g. consideration of standard states for SLE calculations, the Lewis-Randall/McMillan-Mayer framework or how mixed solvents are considered
- Can the comparison of the various approaches give us an insight on which is the best model development/parameterization method and ideal validation approach ?
- Can the comparison of the various approaches give a clear picture of the physical significance of the various contributions of the e-EoS and their interplay and how this interplay e.g of physical and electrostatic terms changes with temperature and composition ?

In an attempt to provide convincing answers to these questions, the rest of the manuscript is structured as follows. Section 2 gives an overview of the models considered in form of representative summary tables which are briefly presented, but mostly discussed together with more information about a number of models in sections 3 and 4. These sections present, respectively, the e-cubic EoS and the e-CPA equations of state. New results and recent insights on e-CPA are shown in section 5 which ends with some comments on e-SAFT approaches, while section 6 is the overall discussion where input from all previous sections is considered together and where the aforementioned questions are answered (or attempted to). We end with a short conclusion section.

2. Overview of e-cubic/e-CPA Equations of State

The main models we consider here are shown in Table 1, together with their original references. Follow-up works will be presented later. Impact shown in form of citations is also included in Table 1. While all models will be discussed in detail in sections 3 and 4, we summarize their main characteristics in Table 2, and details about their parameter estimation and applicability are shown in Tables 3 and 4. The content of Tables 3 and 4 is not based solely on what is reported in the original publications of the models (as shown in Table 1) but also on follow-up works which are discussed later. Moreover, other versions of the electrolyte CPA approach (beyond the 4 ones shown in Table 1) will be discussed in section 4. Finally, Table 5 presents some characteristics which constitute a deeper analysis of the models and discusses which models have undergone this deeper analysis.

The short overview of Tables 1-5 already illustrates, even among this limited number of e-EoS, that no approach has been based on exactly the same principles, developed in the same way or validated/applied in ways, which could permit easy comparisons of the models. These characteristics pose difficulties in the comparative presentation and analysis of the various models which would permit us answering the questions stated in the introduction. For this reason, we present first in sections 3 and 4 the key features of each approach (with very few equations). In section 5 a more extensive discussion of e-CPA will provide an insight of various model development approaches. We will refer again to these tables (1-5) in section 6 where a broader discussion of all considered models will be presented.

Table 1. Overview and citations of the models

Model	Reference	Citations (25/10/2021)	Citations/year (25/10/2021)	Comments
eSRK-SP	Simon et al., 1991, [13]	19	0.6	No follow-up
eALS	Aasberg-Petersen et al., 1991 [14]	82	2.7	Significant follow-up, see section 3
eCubic	Fürst and Renon, 1993 [15]	141	4.9	Follow-up by Furst, Zuo et al. [34-36] (11-25 cit. per article)
eCPA-WuP	Wu and Prausnitz, 1998 [16]	116	4.8	No follow-up
eSRK-MWS	Myers,Wood,Sandler,2002 [17]	107	5.4	In Lin et al. [19] Comparison to other models
eCPA-IFPEn	Inchekel et al., 2008 [18]	41	2.9	Limited in own group
eCPA-Lin	Lin et al., 2007 [19]	55	3.7	
eCPA-DTU	Maribo-Mogensen et al.,2015 [20]	48	6.9	Significant follow-up, in general of the e-CPA concept, see section 4 (both DTU, IFPEn, Infochem-KBC)

Abbreviations used in models:
SP: Simon-Prausnitz
ALS: the cubic EoS (from the work of Adachi, Lu and Sugie, 1983) used in the eALS model described in ref. 14
WuP : Wu-Prausnitz
MWS: Myers-Wood-Sandler
IFPEn: Institut Francais du Petrole – Energies Nouvelles
DTU: Technical University of Denmark

Table 2. General presentation of the models' characteristics

Model	**Physical term**	**Ion-Ion**	**Born term included**	**Dielectric constant Or Relative Permittivity**	**Ion-based**
eSRK-SP	SRK	PDH	yes	= f(T,V,i)	Yes
eALS	ALS	DH	no	=f(T)	No
eCubic	Cubic+SR2	iMSA	no	=f(T,i)	No
eCPA-WuP	CPA	iMSA	yes	=f(T,i)	Yes
eSRK-MWS	PR	eMSA	yes	= f(T,V)	No
eCPA-IFP	CPA+SR2	iMSA	yes	= f(T,V,i)	Yes
eCPA-Lin	CPA	MSA/DH	Yes	=f(T, V)	Yes
eCPA-DTU	CPA	DH	Yes	= f(T,V,i)	Partially

Abbreviations used in models:

PDH = Pitzer-Debye Hückel

SR2 = short-range ion interaction term in the Fürst-Renon model (this model uses either this term or Born, but not both simultaneously; SR2 term is not used any more in this model)

DH= Debye-Hückel

MSA = Mean Spherical Approximation (i=implicit; e=explicit)

T, V, i: Temperature, Volume, ion concentration dependency

Table 3. Parameter estimation of e-EoS. See footnotes of Tables 1 and 2 for presentation of models and explanations of abbreviations.

Model	**Ion-association**	**Max molality mol/kg water**	**T-range (C)**	**Number of salts (mixed) – other solutes**	**Fitted parameters in the electrolyte part**
eSRK-SP	-	Sol.limit	0-80	2(0)-1	Ion radius + kij ions/water
eALS	-	4	25-120	2(0)-3	Gas/salt and salt/water interactions
eCubic	-	6	-15 – 25	28(30)-2	6 parameters for all salt-water systems considered (28 water-halides)
eCPA-WuP	Ion-solvent	6	0-300	1(0)-1	3 for ions-water + 1 more for mixed solvent
eSRK-MWS	-	8	0-300	7(2)-0	3 salt (2 size and 1 energy)) at 25 C + 6 salt specific parameters at

					high temperatures
eCPA-IFPEn	-	6	25	10(0)-0	2 for ions-water + kij for ions-water or a short-range ion-water interaction
eCPA-Lin	-	Sol-limit	25	5(6)-0	3 per ions + kij for water-ions
eCPA-DTU	-	6	-30 -275	54(5)-5	3 salt/ion-water interactions and 1 more for salt-solvent and salt-gas interactions

Table 4. Applications of e-EoS. See footnotes of Tables 1 and 2 for presentation of models and explanations of abbreviations.

Model	**Mean ionic Act.coef.**	**Osmotic Act.Coef.**	**SLE (salt solubility)**	**Density**	**LLE**	**Gas/salt**	**Mixed solvent**	**Other**
eSRK-SP	yes (25)	-	Yes (mixed solvent, water-ethanol)	-	-	-	yes	NaCl-ammonia-water
eALS	-	-	-	-	-	yes	-	7 gas/salt 2 salts Gas/brine
eCubic	-	yes	-	-	-	-	-	30 salts
eCPA-WuP	yes	-	-	-	-	yes	-	NaCl-water (-methane) 125 C 100-600 bar
eSRK-MWS	yes	yes	-	yes	-	-	-	25 C and higher T
eCPA-IFPEn	yes	yes	-	yes	-	yes	-	10 water-salt
eCPA-Lin	yes	yes	yes	yes	-	-	-	
eCPA-DTU	yes	yes	yes	yes	yes	yes	yes	

Table 5. Further/deeper analysis of e-EoS. See footnotes of Tables 1 and 2 for presentation of models and explanations of abbreviations.

Model	**Analysis of terms**	**Single ion activity coefficients**	**Other theoretical analysis or special issues in parameter estimation**	**Comments**
eSRK-SP	yes	-	-	Very few systems
eALS	-	-	Use of low P gas/salt constants for predictive calculations	
eCubic	-	-	Interrelation between energy and size parameters of ions is investigated	
eCPA-WuP	-	-	Ion-ion association Sites on ions	LR/MM analysis – discussion, no conclusion
eSRK-MWS	-	-	-	LR/MM analysis – discussion, conclusion is that importance of such corrections is small
eCPA-IFPEn	yes	-	-	
eCPA-Lin	-	-	Various parameter estimation methods studied	
eCPA-DTU	Yes	Yes (in later studies)	Wide range of properties studied	

LR/MM: Lewis-Randall/McMillan-Mayer framework analysis

3. The electrolyte Cubic Equations of State (e-EoS)

3.1 The Simon – Prausnitz model (1991) [13]

The Simon & Prausnitz EoS from 1991 combines the SRK model for physical interactions with the Pitzer-Debye-Hückel (PDH) term for ion-ion, ion-dipole and dipole-dipole effects as well as a Born-type term for solvation. Only 5 ions are considered (Na+, Cl-, OH-, Mg2+, NH4+) and critical properties, acentric factors and diameters are obtained from Argon/Neon, except for NH4+ where they are taken from ammonia. The dielectric constant of solvent mixtures is calculated from the Buckingham model and then corrected for and extended to ions.

The model has only two fitted parameters; ion radius and kij (interaction parameter) between ions and water. They are fitted to mean ionic activity coefficients of NaCl-water and MgCl2-water at only one T (25 ^{o}C) with very good results. For NaCl-water an interesting term analysis is shown, with the Born and Debye-Hückel terms showing large and opposite results (positive and negative, respectively) to the activity coefficients. This early discovery was later verified for many other models, as shown in literature when Born term is included with a composition dependency [see e.g. 18, 21-23]. The SRK contribution is rather small over the whole concentration range.

The solubility of NaCl in the mixed solvent water-ethanol is shown at 28 °C – this is pure prediction and the results are excellent (ion-alcohol kij is apparently zero, this is not entirely clear). Also acceptable results are obtained for NaCl/ammonia/water. The authors refer to new data to appear soon for a more complex multicomponent system (water-methanol-ammonia-NaCl-N2), but this does not appear to have taken place.

Discussion

The work of Simon and Prausnitz presents an early development of an ion-specific e-EoS and is both exciting and pioneering at its time in many respects. It considered mixed solvents, the Born term (long before it has become more extensively used in e-EoS, as discussed later), it contains an analysis of the various terms and even a dielectric constant which is a function of both temperature and composition. Whether the derivatives of dielectric constant with composition have been considered in obtaining the activity coefficients is not easy to conclude. Only two ion-related parameters are needed and the very good mixed solvent results are predictions. It appears that both Born and the ion-ion term (Pitzer-Debye-Hückel, PDH) are equally important, while the physical part is small. Some of these conclusions will be verified via other EoS and other electrolyte models 20-30 years later [18,21-23].

On the negative side, all results are shown at just one (room) temperature and there has never been, to our knowledge, any follow-up of this work by the same or other researchers. Thus, calculations for e.g. densities, LLE, salt solubilities, thermal properties or at other conditions e.g. higher temperatures have never been presented.

3.2 The Aasberg-Petersen and Stenby model (1991) [14]

Before the Aasberg-Petersen & Stenby model

Before presenting the work of Aasberg-Petersen and Stenby [14], it is relevant to discuss the predecessor, the model proposed by Harvey and Prausnitz (1989) [24], which is actually a combination of a non-cubic EoS with electrolyte terms, but with the same focus i.e. high pressure water-gas-salt systems. In this excellent paper, Harvey and Prausnitz present this new (at the time) e-EoS by combining a physical term (a somewhat complex one containing hard-sphere and perturbation contributions; the so-called Barker-Henderson model), with two electrolyte terms; a Born-type and the explicit MSA. The latter implies an average diameter for all ions but it was shown to be quite good compared to the full MSA in a previous publication [25].

The model parameters are:

- The Lennard-Jones energies (function of temperature) and diameters in the physical term for water, gas and hydrocarbons
- One ion (salt)-water and ion(salt)-gas cross energy parameter

- The gas-water cross energy parameters as function of temperature in the physical term of the model

The Lennard-Jones energies and diameters of ions are taken from literature or predicted (the energies) from the Mavroyannis equation (as function of polarizabilities and valencies). More specifically, the ion-dispersion energy is calculated from the following equation, using the average ion polarizability (α_i), total electron number on the ion (n_e) and Pauling ion diameter, σ_i (all parameters taken from the literature):

$$\frac{\varepsilon_i}{k} = 356\frac{\alpha_i^{1.5}\sqrt{n_e}}{\left(\sigma_i/2\right)^6} \tag{1}$$

The Born equation has the role to keep the ions in the liquid phase and employs the dielectric constant as function of T,P and composition using an expression from the same authors from 1987 [26], but it is unclear to us whether all the compositional derivatives are used in the estimation of activity coefficients.

The salt-water cross energy parameter is obtained from osmotic activity coefficients at 25 °C, and good results are shown for NaCl-water; possibly also good for the other 7 salt-water systems considered. The gas-salt cross energy parameter is taken from the Setchenow coefficients at 25 °C. No other temperatures are considered in the work.

We can conclude that the proposed approach is overall an ion-specific model with salt-specific parameters for water-salt and gas-salt interaction energies.

The results shown are all pure predictions for water-gas-salt at all pressures. In general terms the agreement is good, at least in qualitative terms but not quantitatively in all cases. There are some very good results even for two brine-natural gas systems. There is, however, a systematic underestimation (often rather severe) of the salting-out effect, less for CO_2-NaCl (150 °C), more severe for all other cases ($CaCl_2$, NaCl + other gases, even more pronounced at 4 or higher salt concentrations).

Discussion

This is an excellent manuscript [24] and Harvey and Prausnitz attempted to find explanations for the not-so-good results reported in some cases. They looked at all possibilities e.g. the primitive model concept, the physical model choice (there are deviations for non-salt systems e.g. methane-water and CO_2-water esp. at high pressures), not considering the hydrogen bonding & structure of water, whether MSA is off, and the role of parameters (adjustable parameters of LJ type) or effect of regression at 25 C and how it affects the results at high temperatures. It was a very nice discussion without any real conclusion on which factors are the most crucial for the not-so-good results.

In general terms, we can conclude that the approach of Harvey and Prausnitz is interesting with some promising elements but it has not been tested for mean ionic/osmotic activity coefficients or water activities at high temperatures, neither for many systems, so in that sense it is not a complete model. The model choice for the physical term is possibly poor and a more advanced EoS or an association model would do much better. Today we know that gas-water systems can be described much more accurately. The use of Born term is certainly worth mentioning including a dielectric constant expression which seems complete (function of T,P, composition) but it has not been fully discussed, neither was analysed the relative contributions of the Born and MSA terms (vs. also physical part). It was a very good idea to use the Setchenow constants for gas-salt systems, as this permits the model to maintain a semi-predictive character (such constants are available for some systems and then the model can be used for predictions for gas-water-salt, once these constants are used to estimate the gas-salt cross energy interactions).

The Aasberg-Petersen and Stenby approach [14]

Aasberg-Petersen and Stenby proposed in 1991 [14] a salt-specific EoS where the emphasis is on the effect of salts on gas solubility in water at higher pressures, which are important for oil & gas related applications. No other applications are considered or intended and as such the model is not of general applicability. No ions are permitted in the gas phase and this is an in-built assumption of the model. The model is based on the following equation which includes the fugacity from an EoS for the physical part and the electrolyte activity coefficient model. This equation has been used with various choices for EoS by other authors, as we will see later:

$$ln\Phi_i = ln\Phi_i^{EoS} + ln\gamma_i^{elect} \qquad (2)$$

where *EoS* represents the physical model and *elect* is the electrolyte term (taken from a form of the DH theory). In the 1991 work, the EoS in the physical term is given by the so-called ALS cubic EoS (which includes a rather strange mixing rule for the energy parameter). The physical term (EoS) includes the gas-water interaction parameters (three in total per gas) and the electrolyte term contains a single salt-non electrolyte (water, gas) parameter ($h_{i,salt}$).

Two approaches have been followed to fit the $h_{g,salt}$ i.e. the gas-salt interaction parameters needed in the electrolyte term:

i. using the ternary gas-water-salt data (this is of course pure correlation with little interpretative value)
ii. using the low pressure salting-out constants which are relatively easily obtainable from experiments (this we could call, with a bit of good will, prediction)

The approach (i) has been used for 4 systems and the approach (ii) for 7 systems (at 298 and 323 K). Almost equally good results are obtained with both approaches, (i) and (ii), for N_2-NaCl-water, Methane-NaCl-water, CO_2-$CaCl_2$-water, Methane-$CaCl_2$-water and a natural gas-brine system.

The general applicability of the model is limited, as previously mentioned e.g despite the availability of parameters, the EoS has never been tested for activity coefficients (mean ionic, osmotic or water) for the two water-salt systems considered!

Nevertheless, the results are better than the Harvey-Prausnitz EoS from 1989, considered at the time to be a very good model for gas solubilities, with the improved results ascribed to the better model for the physical effects (salt-free systems like methane-water).

There has been a very extensive follow-up work by many researchers who used the same approach as Aasberg-Petersen and Stenby, mostly with other EoS in the physical term. Maddox [27] used the same ALS EoS (and PR) but now the h_{ws} is both pressure and concentration dependent. They applied their model to hydrate curves of CO_2 (or H_2S)-electrolytes-chemicals (alcohols, glycols, glycerol). Kang in 1998 [28] used eq. 2 with SRK and Pitzer, again for hydrate curves for CO_2 or methane- with MgCl2-water. Ziaee in 2015 [29] used eq. 2 with CPA EoS and PDH for H_2S/CO_2-water-methanol-HCs (there are no salts involved here but reactions are considered for H_2S/CO_2 and water). Finally, in the Heriot-Watt group (Professors Tohidi and Chapoy and co-workers), eq. 2 has been used in a series of publications: In 2003 [30] eq. 2 is used with the VPT EoS and strange mixing rules but NO electrolyte term and rather strange large kij values where salts are considered components in the EoS (this is essentially a correlation exercise). In their 2008 and 2009 papers [31-32], they use the full version of equation 2 with CPA for the physical term and the same approach (PDH) as Aasberg-Petersen and Stenby for the electrolyte term. Methane hydrate terms are calculated for methane in aqueous mixtures of NaCl, $MgCl_2$, $CaCl_2$, NaCl+KCl with the h_{sw} being a function of T and salt concentration with 5 parameters obtained from freezing point depression data.

In brief, all the above follow-up approaches of the Aasberg-Petersen and Stenby method are rather empirical salt-specific approaches, typically used and actually designed for gas hydrate systems, with a water-salt interaction parameter which appears to be highly empirical and strong function of several of the following: T, P, salt concentration. They have some correlative value, they are not general models and even lack the interpretative value of the original Aasberg-Petersen and Stenby approach (where in some cases semi-predictive results were obtained).

3.3 The Myers-Wood-Sandler model (2002) [17]

Myers et al. (2002) [17] developed a general salt-specific e-EoS (abbreviated here as MWS) by combining the translated PR EoS with an explicit primitive MSA (for ion-ion interactions), as obtained from Harvey et al. (1988) [25], and the Born term. They used the restrictive primitive model version of MSA where all ion diameters are assumed to have the same values.

Pure water is described with three temperature-dependent parameters to ensure good representation of vapor pressures and liquid densities.

In the Born and the MSA terms a constant value is used for water's dielectric constant, ignoring the effect of salt concentration and temperature. Thus, the Born-term has no effect on the mean ionic activity coefficients, only on the Gibbs energy of hydration. In the Born term, higher values of diameters are used (0.1 Å higher for the anions and 0.85 Å higher for the cations compared to bare ion values).

The equation has also a volume translation but this is not used for salts and, moreover, the interaction parameter k_{ij} between water-ions is set to zero. Thus, the MWS EoS has three salt-specific parameters (the energy and co-volumes as well as the diameter) which are fitted to activity coefficient data at 25 °C. Of course co-volumes and diameters are expected to be linked but this link is not used by Myers et al. [17].

Myers et al. (2002) [17] applied their model to 138 water-salt systems (and a few mixed salt-water ones), first of all at room temperature and they considered mean ionic and osmotic activity coefficients. With three adjustable parameters per salt, very good representation is achieved (deviations around 2%), even at much higher molalities (>6 mol/kg) than those used in the parameter estimation, sometimes even up to molalities of 15 mol/kg. As the model is salt (and not ion-) specific the fit of the data is easier and is not done simultaneously for all salts.

As something different from most other studies, they considered the transformation needed between the Lewis-Randall and McMillan-Mayer frameworks (used in the cubic EoS and ion-ion parts, respectively), but they found that the differences were small and bound to be compensated by the adjustable parameters.

What is required for calculations at higher temperatures

Unlike many other EoS of that period (including the Fürst and Renon, discussed next), Myers et al. were “bold” enough to consider the higher T and P and it is clear that this was not an easy task.

The MWS EoS was used for modeling densities, osmotic and mean ionic activity coefficients at higher temperatures for 7 water-salt systems, but then both the energy parameters and the diameters are made temperature-dependent and a non-zero interaction parameter between water-salt is required (high values: 0.2….-0.4). In total, there is a need for 2 parameters for each salt-water system fitted to mean ionic and osmotic activity coefficients as well as densities.

The representation is satisfactory in the 0-300 °C and 1-120 bar temperature and pressure ranges by employing 6 adjustable salt-specific parameters. It is possible to reduce somewhat the number of adjustable parameters by utilizing a correlation between the salt’s co-volume and diameters.

A few mixed salt (NaCl+LiCl, NaCl+$CaCl_2$) osmotic activity coefficients have been considered with satisfactory results.

There has been very limited future work on the MWS EoS by the developers despite promised to do so in the 2002 paper [17]. The authors discussed also the importance of partial dissociation and ion pairs at higher T and ion concentrations but this was not considered in their work. A single short follow-up paper by the authors in 2003 [33] focused on dilute solutions NaCl-water at near critical water conditions. The MWS model has never been developed by the authors as ion-specific.

Further studies

A few years later, Lin et al. (2007) [19] further tested the MWS EoS using either the simplified explicit or implicit versions of MSA. They used an ion-specific version of MWS, with three adjustable parameters for ions (the energy and co-volume parameter of Peng-Robinson as well as the ion diameter). The volume translation is zero for ions. They also employed a k_{ij} for interactions between ions. The Lin et al. version of MWS EoS is tested for multicomponent systems containing water, Na^+, H^+, Ca^{2+}, Cl^-, OH^- and SO_4^{2-} and a variety of properties (mean ionic and osmotic activity coefficients, apparent molar volumes and SLE). The performance of MWS was similar to the more advanced EoS they compared their results to but we will return to this in the next section when discussing the electrolyte CPA equations of state.

3.4 The Fürst-Renon model (1993) [15]

Fürst and Renon (1993) [15] proposed the first well-organized and extensively used electrolyte EoS which has been widely applied to many electrolyte systems and diverse conditions. It is a salt-specific model based on a modified SRK EoS for the physical interactions, the simplified implicit MSA for ion-ion interactions and the so-called SR2 term. The latter has a central role in the model and represents the short-range ion-solvent interactions. The SR2 term has not been used by many groups in the area.

The water's diameter is set to 2.52 Å in both the MSA and SR2 terms. The model has, in principle, three types of parameters; the ionic co-volumes and the ionic diameters as well as the W_{ik} parameters in the SR2 term. The ionic co-volumes and ionic diameters are correlated:

$$\sigma_i = \left(\frac{6b_i}{\pi N_A}\right)^{1/3} \text{ or equivalently } b = \tfrac{1}{6}\pi\sigma^3 \qquad (3a)$$

The interaction parameters (W) between anions (aa), between cations (cc) as well as between anions and water (aw) are set to zero (due to the lower solvation of anions), leaving only the cation-anion (W_{ca}) and cation-water (W_{cw}) interaction parameters to be determined from experimental data.

In the original paper [15], Fürst and Renon considered osmotic activity coefficients for binary and ternary (mixed salt)-water mixtures. Using experimental osmotic coefficients for numerous halide solutions (Cl^-, Br^-, I^-), Fürst and Renon showed that the co-volumes and interaction parameters in their EoS are strongly correlated and they can be related to the Stokes diameter for cations (σ_c^S), the Pauling diameters for (the less-solvated) anions (σ_c^P), or their combinations using the following relationships:

$$b_c = \lambda_1\left(\sigma_c^S\right)^3 + \lambda_2$$

$$b_a = \lambda_1\left(\sigma_a^P\right)^3 + \lambda_2 \qquad (4)$$

$$W_{cw} = \lambda_3\left(\sigma_c^S\right) \ + \lambda_4$$

$$W_{ca} = \lambda_5\left(\sigma_c^S + \sigma_a^P\right)^4 + \lambda_6$$

When these equations are used, the model is essentially (semi)predictive (naturally the λ_i-parameters are fitted to experimental data). For the 28 aqueous halide solutions considered in the 1993 article [15], the percentage deviation is 2.6% for the osmotic coefficients, when the above equations are used, but it is reduced to 1% when a single parameter for the cation-anion interaction (W_{ca}) is adjusted whereas all other parameters are given by the generalized equations.

With few exceptions, equally satisfactory results are obtained for other salts (containing anions other than Cl^-, Br^- and I^-) but improved results can be achieved if special parameters λ_5, λ_6 are fitted for each anion family together with the W_{ca}-parameter. Even better results can be obtained when the anionic diameter is adjusted as well. Using solely parameters from the binary water-salt systems, the Fürst-Renon EoS predicts very satisfactorily the osmotic activity coefficients for 30 mixed salt-water systems. Typically the deviations in osmotic coefficients range between 2 and 5%.

Further studies and discussion

Later, Zuo et al. (2000a,b) [34,35] applied the Fürst and Renon e-EoS with some success to VLE, activity coefficients and LLE for various mixed solvent-water mixtures. VLE for 31 mixed solvent-water mixtures and LLE for 13 mixed solvent (water-butanols, water-ketones) – salts (NaCl, KBr, KCl) have been considered. Others e.g. Vu et al. (2002) [36] have applied the model also to hydrate systems.

In many respects, the Fürst and Renon e-EoS opened the way for many of the e-EoS that followed. The efforts of the authors to make several plausible assumptions for reducing the number of parameters are commendable. So are the subsequent works where the model has been extended to both aqueous and non-aqueous systems, including both mixed solvent VLE and LLE calculations. The predictive value of the models in these multicomponent systems is highly questionable but even up to this date, such calculations are very difficult. Whether the SR2 term is of real importance has not been clarified but this issue has been followed up by Inchekel et al.(2008) [18] in their e-CPA discussed later. On the negative side is that neither Fürst and Renon nor other authors have seriously considered the high temperatures and SLE (salt solubilities). Finally, the model has never been further developed as an ion-specific model. The Fürst and Renon is today a model of mostly historical value but with very important lessons learnt also about the interrelation of ion/salt size and interaction parameters. A careful study of this model indicates that such parameters may be difficult to be determined independently of each other in electrolyte equations of state.

4. The electrolyte Cubic-Plus-Association (CPA) Equations of State (e-CPA)

There have been several versions of e-CPA over the years. The first one has been proposed by Wu and Prausnitz (1998) [16], only two years after CPA has been published by Kontogeorgis et al., 1996 [37]. The IFPEn version by Inchekel et al. [18] has been published 10 years later (2008) and about that time also the model by Lin et al. (2007) [19], which is the first version of e-CPA from our group at DTU. In addition, a special version of e-CPA has been developed by Infochem/KBC [44-46] and there have been e-CPA versions following the approach of Aasberg-Petersen and Stenby.

These versions of e-CPA are presented in this section under "earlier studies".

More recently, after 2015, a more systematic version of e-CPA from DTU has been published, first by Maribo-Mogensen et al. (2015) [20] and later by others [38-43] who have continued and further developed and validated the model. These models are also presented next after the "earlier studies" and further discussed in the subsequent section.

All the e-CPA models are based on the CPA EoS for the physical term, either using SRK or PR for the non-associative interactions. In most (but not all!) of the approaches, the association term is used only for water (and other hydrogen bonding solvents). Besides that, the models differ significantly, as will be explained during their presentation. Some of the approaches have used MSA for ion-ion interactions (implicit forms of MSA, which do not assume the same ionic diameter) and they are ion-specific models. Other versions have used the full or other version of the Debye-Hückel equation and can be partially salt-specific models. All/most of the aforementioned models used the Born term but in different ways, as we will explain later.

Finally, we should mention that we limit our discussion to systems of strong electrolytes e.g. salt solutions. There are more applications of e-CPA and e-Cubic models for weak electrolyte systems e.g. aqueous alkanolamine solutions of relevance to CO_2 capture, see ref. [2] for a review of some of these models and ref. [105] for a recent application.

Earlier studies on e-CPA

4.1 The e-CPA of Wu and Prausnitz (1998) [16]

The Wu and Prausnitz (1998) [16] e-CPA is based on the combination of the PR EoS and the association term of SAFT, with the complete implicit MSA (one of the very few models to our knowledge that used the complete MSA version) as well as the Born term.

Water is modeled using the three-site (3B) scheme, but the association term is not used just for water. Unlike most other e-EoS models, this version of e-CPA employs association between water and ions (assigning 10 sites for cations and 14 for anions). This water-ion association approximates the electrostatic interactions between water and ions. Although this association between cations and ions (Na+/Cl-) was used by Wu and Prausnitz [16] in their e-CPA, we must emphasize that the applicability of this model is limited to just one system (NaCl+water and ternary with methane), even though temperatures up to 300 °C were considered. Moreover, the values chosen for the number of sites associated with ions seem rather high e.g. when compared to the hydration numbers of Na^+ (=6) and Cl^- (=7).

The ionic co-volumes, b_i, are not separate parameters but they are linked to ionic diameters, σ_i via an equation similar to equation (3a), i.e. a similar same approach as used in the Fürst-Renon equation of state. However, in the case of the Wu-Prausnitz e-EoS the exact relationship is:

$$b = \frac{2}{3}\pi\sigma^3 \tag{3b}$$

which actually implies a co-volume much larger than the one indicated by equation (3a). According to eq. (3b), the co-volume is about 4 times the ionic volume (assumed spherical), while in eq. (3a), the co-volume is about equal to the ionic volume. Both equations (3a) and (3b) have been used in other e-EoS. We will return to the co-volume/ion diameter relationships later in this review.

The e-CPA by Wu and Prausnitz contains 3 adjustable parameters for ions (the acentric factor is zero; the association volume=0.001 for all ions). The energy and co-volumes are calculated from correlations with the (Lennard-Jones) energy and diameter (Mavroyannis equation (1) mentioned above), but the association energies of Na^+ and Cl^- are fitted to water activities and mean ionic activity coefficients. Mixed solvents require an additional fitted parameter (see below).
As mentioned, the e-CPA by Wu and Prausnitz has been applied to water-NaCl (water activity and mean ionic activity coefficients) as well as the water-methane-NaCl system (gas solubilities). In the case of the mixed solvent, the concentration dependency of the dielectric constant D is considered (shown by the empirical equation below, eq. 5), and in this case the Born term influences the phase equilibria calculations:

$$\frac{1}{D} = \frac{1}{D_w}\left(1 + k_D x_{HC}\right) \tag{5}$$

where w=water, HC=hydrocarbon, k_D is a dimensionless constant that depends on the hydrocarbon (and is a parameter fitted to solubility data).

The solubility of methane in pure water and at molalities 1 mol/kg and 4 mol/kg in aqueous NaCl solutions at 125 °C has been presented graphically by the authors. The correlation results are satisfactory up to high temperatures (300 °C) even though the description of the alkane solubility in water and water-methane VLE are not very satisfactory. The latter indicated according to the authors problems due to the hydrophobic effect, but today we know that water-alkanes can be represented very well with CPA and SAFT models with a more appropriate parameter estimation [2].

Discussion

In conclusion, there is some merit in the overall approach by Wu and Prausnitz, but the applications were limited to a single solvent and VLE/activity coefficients and some gas solubilities (salting-out) calculations. There are no applications for other salts, for salt solubilities and LLE calculations and there has never been a follow-up of the approach by these authors or others.

It is difficult to determine from this study the importance of assigning association to ions. It would be useful to establish whether the developed correlations can be used for estimating the parameters of other ions, including the association parameters. Moreover, the novelty of the water-ion association needs further study. 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.

4.2 The e-CPA of the IFPEn group (Inchekel et al., 2008) [18]

The e-CPA by Inchekel et al. (2008) [18] combines an SRK-based CPA with the simplified implicit form of MSA (non-restrictive to same ion diameter), the Born term and an additional term, the so-called SR2. The latter is identical to the term used by Fürst and Renon in their e-EoS and is used to represent the short-range ionic interactions.

Water is modelled as a 4-site molecule in the CPA part (4C-scheme), but unlike Wu and Prausnitz [16], there are no sites in ions and no water-ion association. Thus, the association term is only used for water.

The relationship between ionic diameters and co-volumes is given by the same equation as in the Fürst-Renon equation (equation 3a).

The IFPEn e-CPA contains two ionic parameters (SRK's energy parameter and the ionic diameter) as well as binary interaction parameters (k_{ij}) between water-ions (other k_{ij}'s are zero) or the W_{ij} interaction parameters of the SR2 term.

Finally, this e-CPA includes an investigation of SR2 and Born terms for accounting for short-range and solvation effects, as well as the (rather empirical) Pottel and Simonin expressions which are used for the dielectric constant-concentration (and temperature) dependency:

Pottel:

$$\varepsilon - 1 = (\varepsilon_s - 1)\frac{2(1-\xi_3)}{2+\xi_3} \tag{6a}$$

Where the parameter ξ_3 is defined as:

$$\xi_3 = \frac{\pi N_A}{6}\sum_i \frac{n_i \sigma_i^3}{V} \tag{6b}$$

The summation in ξ_3 for use in the Pottel equation is over ions alone. The solvent relative permittivity or dielectric constant (ε_s or D) can be calculated from equation shown below (eq. 6d).

Simonin (containing an adjustable parameter α):

$$\varepsilon = \frac{\varepsilon_s}{\left(1+\alpha\sum_{ions} x_i\right)} \tag{6c}$$

In both expressions ε_s is the solvent's e.g. water's relative permittivity (dielectric constant). This is usually taken from literature expressions, as a function of the temperature and density. For mixed solvent systems, it can be shown that the dielectric constant D of liquid mixtures can be approximated as the volume fraction average of the dielectric constant of the pure compounds:

$$D = \frac{1}{V}\sum_{i=1}^{NC} V_i D_i \tag{6d}$$

where V_i and D_i are the pure component volume and dielectric constants of pure solvents e.g. of water and alcohol.

The e-CPA by Inchekel et al. has been applied to mean-ionic and osmotic activity coefficients at 25 °C and apparent molar volumes of 10 aqueous salt solutions (up to molality of six mol/kg). Salt solubilities, high temperature calculations, thermal properties and LLE are not considered.

The correlation results are satisfactory and it is concluded that the preferred approach is to use the Born term with the Simonin dielectric constant expression, which includes an additional adjustable parameter.

The optimized ionic diameters are larger than the Pauling diameters but they have reasonable values and follow the expected trends for the cations and anions considered (see discussion in section 6 where ionic diameters from other models are also presented).

Excellent results are obtained by using the same ionic diameter values in all expressions where the diameter enters (MSA, SR2, Born), although this is somewhat in contradiction with the physical meaning of the diameter in these expressions.

Best results are obtained when solvent-ion k_{ij} parameters are used (in the attractive part of SRK), rather than with the W_{ij} parameters in the SR2 term, especially for the apparent molar volumes (osmotic activity coefficients are less influenced by the approach used). Except for K^+ and Mg^{++}, all the other ion-water k_{ij}'s are negative, of the order -0.4.

Finally, as something particularly interesting, for two salt-water mixtures, a relative analysis of the various electrolyte terms is performed. It can be seen that the Born contribution is positive and nearly counterbalances the (negative) MSA contribution; thus appearing to be significant in the analysis. If the dielectric constant is assumed to be (salt) concentration independent, then the Born term does not contribute to the activity coefficients. There is hardly any contribution from the association term. These conclusions appear to be similar to those obtained in the other similar earlier analysis we have mentioned by Simon et al. (1991) [13]. According to Inchekel et al. (2008) [18], 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. We return to the topic of the analysis of the terms of e-EoS later in this review.

The same group [106] and others [104] have further developed and applied electrolyte CPA with success for very high temperature and pressure NaCl-water-gas (methane, CO_2) systems at pressures up to 200 MPa and temperatures up to 773 K. This version of e-CPA in these references

[104, 106] includes MSA and Born (no SR2 terms) with Simonin's expression for the concentration dependent dielectric constant. All ion-size parameters (in the Born, MSA and physical terms) are the same and the co-volume and ion-size parameters are connected via the simple expression mentioned above ($b = \frac{1}{6}\pi\sigma^3$). Water is a four-site molecules and Na+ and Cl- ion-size parameters as well as two energy parameters in the Soave temperature dependent energy expression are fitted to vapor pressures, volumes, osmotic and mean ionic activity coefficients for NaCl-water. The correlation is very successful over the extensive T-ranges mentioned above. Using kij parameters, with quadrative T-dependency, between the gases (methane, CO_2) and NaCl, good results are obtained also for the phase equilibria of the NaCl-water-gas systems (about 30% deviation for pressures and volumes both in the case of methane and CO2).

4.3 The e-CPA of Lin et al. (2007) [19]

Lin et al. (2007) [19] published the first electrolyte version of CPA developed at DTU. In the same publication, they considered electrolyte cubic EoS as well as a version of the Myers et al. EoS [17].

Their e-CPA uses the simplified implicit MSA and the Born term. The model contains 3 ionic parameters (the energy and co-volume as well as the ionic diameter; the two latter are, somewhat surprisingly, not connected and both are used) and an interaction parameter, k_{ij} (between water-ions and in some cases also between ions). Lin et al. (2007), and this is a significant novelty compared to all other models discussed in this section, considered mixed salts and SLE and they moreover have compared e-CPA results to various other e-EoS previously mentioned. An important characteristic of this study is that they have considered a wide range of properties and parameter estimation approaches.

More specifically, the e-CPA by *Lin et al.* has been developed and tested for the systems containing water and six ions (Na^+, H^+, Ca^{2+}, Cl^-, OH^- and SO_4^{2-}). All the ionic parameters (and k_{ij}) were regressed simultaneously to aqueous electrolyte solutions at 25 °C (VLE, apparent molar volumes, osmotic coefficients and solid-liquid equilibrium data). Over 1300 experimental data points were used. SLE phase diagrams have been presented for 10 ternary mixed salt-water systems e.g. Na_2SO_4+NaCl+water, Na_2SO_4+NaOH+water and $CaCl_2$+NaCl+water (and others containing HCl, $CaSO_4$ and $Ca(OH)_2$). Also are shown apparent molar volumes for various salts and mean ionic and osmotic activity coefficients for various aqueous salt solutions. The performance of this e-CPA is satisfactory but similar to the e-PR tested by the same authors. It appears thus that the association term has a small effect (this term is only used for water). The worse model among those compared by the authors was the e-SRK (especially for the apparent molar volumes) but it must be emphasized that in this e-SRK only an "activity coefficient-type" version has been used with a simplified Debye-Hückel equation.

The authors concluded that simultaneous representation of activity coefficients, apparent molar volumes and SLE requires that pure ionic parameters and interaction parameters between all ions-water as well as certain ion-ion parameters are simultaneously optimized. If SLE data are excluded, the amount of interaction parameters is reduced e.g. cation-water k_{ij}'s=0 and all ion-ion k_{ij}'s=0. Moreover, if only activity coefficients or apparent molar volumes are considered, then the number of interaction parameters can be further reduced e.g. all k_{ij}'s=0.

As mentioned previously, the authors found small differences between the various e-EoS they have tested for the systems they considered, even when different versions of MSA were employed. They found essentially no reason for including the association term, as e-CPA and the versions of the MWS EoS investigated perform very similarly.

The results are overall encouraging and for a wide range of properties. Unfortunately, the values of the water-ion interactions parameters are rather high and moreover two size-parameters are used for ions (co-volume of the cubic EoS, b , and ionic diameters, σ), which must be closely inter-correlated. As discussed later (see section 6), the σ -values are often not in good agreement with experimental values.

In brief, a major accomplishment of the study by Lin et al. is that they considered mixed salts and SLE, something very rarely done in the e-EoS studies. Moreover, they demonstrated that there is 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. This link of data and applications (properties investigated) will also be discussed later.

4.4 The Infochem/KBC e-CPA

This version of e-CPA (presented by Pedrosa et al., 2013 [44] and Carvallo et al. 2015 [45] and also in a recent conference paper [46]) is a version of e-CPA developed by the Infochem/KBC company and available in the Multiflash simulator. Not all details on the model's equations, parameters and estimation process are available but it is based on Infochem/KBC's CPA together with a version of Debye-Hückel and Born equations. The general electrolytes contribution to the total residual Helmholtz free energy includes:

- the Debye-Hückel term that describes the electrostatic ion-ion interactions.
- Born term for interactions between ions and the surrounding medium
- Virial terms for the short-range interactions between the ions.

As mentioned, there is limited information on how the parameter estimation is carried out and how many parameters the model has, but in these publications it has been applied to NaCl (+some other salts)-water-gas (CO_2, Methane) systems.

Especially in the recent conference paper ([46]), as well as in the web-site of the company (www.kbcat.com), more information is provided as well as comparisons of e-CPA with SRK with NRTL/Huron-Vidal mixing rules (and NaCl treated as "pseudo-component"). In this recent study, e-CPA is presented as a combination of CPA, Debye-Hückel (full version presumably) and both a Pitzer-type virial term for short-range ion-interactions and the Born term (using the dielectric constant of solvent, independent of ion concentration). The ion-solvent interactions are represented via the Born term, but only few details are provided on number of parameters and parameter estimation. What is also new in [46] compared to previous publications of the model, is that a very extensive application of e-CPA and the SRK-NRTL/Huron-Vidal models is presented, beyond also the several non-electrolyte systems considered (polar, gas-hydrate inhibitors). The applications considered in [46] included water-NaCl vapor pressure (298-353 K), NaCl, $CaCl_2$, MgCl2 freezing point depression, methane hydrates with NaCl+KCl, NaCl+$CaCl_2$, NaCl+KCl+$CaCl_2$, CO2- Methane hydrates with NaCl, KCl, $CaCl_2$, NaCl+KCl+$CaCl_2$, methanol-NaCl, methanol-$CaCl_2$, methanol-3 salts, natural gas+formation water as well as black oil+formation water.

The authors conclude that good and overall similar results are obtained with both models but eCPA is a bit better (0.5 degree deviation vs. 1 for SRK-Huron Vidal). The e-CPA EoS is especially better for CO_2 hydrates and for the higher salt concentrations and for mixed electrolytes as well as for the salt-alcohol mixtures. It was interesting to see that salts have a stronger hydrate effect than methanol. Thus, overall, e-CPA is recommended compared to SRK-Huron Vidal although the latter model is not bad at all and is also shown to be a simple, rather accurate, fast and robust model (despite being highly empirical of course and with no explicit term for accounting for the ionic interactions).

Discussion

It is a rather special, and somewhat "unique" feature of this e-CPA version that, in addition to the Debye-Hückel and Born terms, it includes a Virial (SR ion) term. Also, unlike the e-CPA versions mentioned above, this version employs DH for ion-ion interactions and not MSA. This topic and comparison of the two ion-ion terms is considered later in this review.

It should be emphasized that the e-CPA version by Infochem/KBC has been developed with oil & gas applications in mind. The principal objective was (Xiaohong Zhang, personal communication) to enable the gas hydrate model of the company to give accurate predictions on hydrate inhibitions when salts are present. The original electrolyte model was developed in conjunction with a cubic EoS using the NRTL/Huron-Vidal mixing rule but later a CPA-based version was also developed. In order to achieve correct thermodynamic solutions, it has been pointed out that solid precipitation models are also required for each salt species, including the different hydrated forms. The electrolyte model parameters of the model are ion specific. The ions included are Na+,

K+, Ca++, Cl- and Br-, but other ions can be added. As mentioned, the model can accurately predict the suppressing effect of the mixed solvents (water, methanol, ethanol, glycols and salts) on hydrate formation, the solubility of gases in electrolyte solutions, the freezing point depression and vapour pressure lowering. The solid precipitation model also allows us to consider halide scales. Especially in the recent publication [46], an extensive list of applications (including mixed solvents, mixed salts, etc. esp. for gas hydrate applications) is considered.
Finally, in another conference paper, Moorwood et al. (2006) [47] addressed several fundamental issues of electrolyte thermodynamics (which may be of relevance also to this version of e-CPA). According to Moorwood et al., the LR/MM conversion effect should be small, and moreover, as the dielectric constant is independent of ion concentration in the charging process, the dielectric constant should be independent of ion concentration and should be only a function of the solvent. This means, according to Moorwood et al., that the Born term will not contribute to the mean ionic activity coefficients and, moreover, the Debye-Hückel term will not include any compositional derivatives of the dielectric constant. On the other hand the authors say that for mixed solvents, the dielectric constant will depend on concentration and thus derivatives with composition will be present in this case. In their view, and without proof, the authors state that these derivatives will have small effect (due to some self-cancelling terms of the derivatives in the Born and Debye-Hückel terms). However, all these statements are provided without results or proof in that study [47].

The current DTU version of e-CPA

4.5 The e-CPA of Maribo-Mogensen et al. (DTU e-CPA) [20]

The e-CPA EoS proposed by Maribo-Mogensen et al. (2015) [20] was a rather special model in a number of ways. The model combines CPA (using the Huron-Vidal mixing rule for the energy parameter) together with the full Debye-Hückel theory and the Born term.

The full Debye-Hückel equation is used for ion-ion interactions, for the first time in this type of models (e-cubic and e-CPA EoS), exactly in the general form presented by Debye and Hückel [48] and also further worked out by Mollerup and Michelsen [49]. This general form of the Debye-Hückel equation gives the possibility to use different “ion-size parameters” for each salt.

The developers had previously showed [50] that the complete versions of Debye-Hückel and MSA theories provide essentially the same results with the composition dependency of the dielectric constant shown to have much more importance and effect on the results rather the choice of the theory for ion-ion interactions (DH or MSA).

Moreover, in this e-CPA model, a theoretical expression for the dielectric constant (as function of temperature and composition) previously developed by the authors [51] is used in both the Debye-Hückel and Born terms of e-CPA. Here it should be mentioned that the decrease of dielectric constant with composition is the sum of two effects, a thermodynamic and a kinetic one (often equally important), and only the former is expected to be captured by or included in thermodynamic models like equations of state. Still, the complete form of the relative permittivity is used in e-CPA.

The e-CPA model of this work [20] is salt-specific in terms of the energetic parameters, but the size parameters (ion diameter and co-volume, linked with an equation identical to that used by Wu-Prausnitz in their version of e-CPA, i.e. equation 3b and the Born radius) are ion-specific and obtained from experimental data for ions/salts and they are not fitted to phase equilibria. Their magnitude is reasonable, and the ion-size parameters from different models are discussed in section 6. In reference [20] are presented ion-size parameters for 17 ions.

The salt-specific energetic parameters of e-CPA ($\Delta U_{ws}^{ref}, a, T_a$) enter the equation for the temperature-dependent energy parameter (between water,w and salt,s):

$$\frac{\Delta U_{ws}}{R} = \frac{\Delta U_{ws}^{ref}}{R} + a\left[\left(1 - \frac{T}{T_a}\right)^2 - \left(1 - \frac{298.15}{T_a}\right)^2\right] \tag{7}$$

These three parameters are fitted simultaneously to mean ionic and osmotic activity coefficients. In addition, at a subsequent step, densities for many water-salt systems are used for fitting a Peneloux-volume correction (T-independent). So, the density data for water-salts have not been included in a simultaneous fit of the energy parameters. The Peneloux-correction only affects the density calculation and not the phase equilibria.

The three parameters shown in eq. 7 and the Peneloux parameters for 54 salts have been presented in [20] over an extensive T-range and molalities (in several cases up to 6 mol/kg).

The e-CPA model by Maribo-Mogensen et al. [20] has been successfully applied to a wide range of applications beyond the data used in parameter estimation. For the mean ionic activity coefficients and osmotic coefficients used in parameter estimation, the average deviations are 5.3% and 3.1% respectively, and for apparent molar volumes it is 1.2%.

In addition, in the original publication [20], good results have been presented for the osmotic coefficients for mixed salts, solubility of salts in mixed solvents (water with alcohols, glycols, alcohols+glycols), gas solubilities (methane and CO2) in water-NaCl as well as water-methanol-NaCl, gas hydrate curves with NaCl+glycols as well as few SLE (salt solubility) calculations (molality over extensive T-ranges). Successful VLE calculations for water-alcohol-salt systems have been presented in subsequent works (M. Bulow MSc thesis, 2017 [52]; Kontogeorgis et al., 2018 [7]). For most of the aforementioned calculations, the salt-water interaction parameters and ion-size parameters, as determined previously, have been used. In some cases, additional parameters are needed. Salt-alcohol and salt-glycol parameters are obtained from ternary data (due to lack of independent information). Moreover, the gas-salt interactions are obtained using the Setschenow coefficients.

There are, however, several issues with the e-CPA model, despite these extensive successful results, as discussed next.

Discussion of the limitations of the e-CPA model by Maribo-Mogensen et al. [20]
First of all, mixed solvent LLE is very difficult to represent. For example, the very complex LLE for water-alcohol-salt systems (sometimes with presence of hydrocarbons) has not been well represented, as shown for several systems both in the 2015 and 2018 manuscripts [20,7].
The LLE 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. For example, as shown by Kontogeorgis et al., 2018 [7], in the case of water-NaCl-1-propanol, while e-CPA correctly predicts a NaCl induced LLE split between water-1-propanol, the driving force for ions towards the 1-propanol phase is extremely weak, possibly due to the neglect of ion-ion association (ion pairs).
While the LLE problems can be attributed to lack of ion-ion association (and presence of ion pairs in systems with low dielectric constants like organic solvents), other problems like with volumetric and thermal properties are attributed to the role of ion-solvent association and water structure.
Another issue are the SLE calculations for mixed salts. Only few such results were shown in [20] and the agreement is acceptable but not perfect. Such data have not been included in the parameter estimation and the standard state properties needed for these calculations for the salts are obtained from another model, the activity coefficient extended UNIQUAC. Using standard-state parameters obtained from another model may not be optimum even if their numerical values appear to be reasonable. This point is further discussed later.
One more issue should be mentioned related to the choices for the density and relative permittivity model used. The latter based on our previous theory [51] provides a relative permittivity value that is both T and density dependent. When a “correct” density for a water-salt solution is used e.g. if we employ the Peneloux translation or experimental value, then the dielectric constant predicted is essentially that of water, i.e. salt-composition independent. This has been also shown in [53]. In this case, the Born term does not contribute (much) to activity coefficients. On the other hand, if we use the e-CPA density for water-salts (without Peneloux), which is shown to be incorrect [20], then the dielectric constant shows the expected decrease with salt concentration. In this case, the Born term will contribute to activity coefficients, but evidently for the wrong reasons (at the cost of sacrificying the density).
Thus, the relative contributions of the electrolyte terms of e-CPA by Maribo-Mogensen et al. [20] may not be correct despite the successful results obtained.
It appears to be a serious issue in this version of e-CPA that all model parameters are fitted to data other than the density and it has been shown in [20] that without the Peneloux term, the model cannot represent the density of water-salt solutions, not even qualitatively correct.

4.6 Follow-up works on DTU e-CPA

Recent studies on e-CPA by Sun et al. [40-43]

Sun et al. in a series of recent publications [40-43] have applied the exact same e-CPA of Maribo-Mogensen et al. [20] to aqueous solutions of tetra-n-butyl ammonium halides [40,41] and gas solubilities [42,43]. Once again the model contains ion-specific size parameters taken from literature and the three salt-specific energy parameters of equation (7) which are fitted to mixture data including ternary water-salt-gas data when such systems are considered.

In references [40,41] the quaternary ammonium salts (halides) are considered. Good correlation results are achieved for activity coefficients (mean ionic and osmotic) at several temperatures and compositions as well as for gas solubilities (4 gases are considered). Densities are good only when the Peneloux volume translation is included. For these organic salt solutions, adding dissociation equilibrium may be of importance due to ion-pairing and hydrophobic effects. It was also observed that not all experimental data are of good quality for such systems.

In the subsequent studies [42,43], e-CPA has been applied to water-salt-gas solubilities for many gases (CO_2, methane, N2, O2, Argon, Air) and for several salts (NaCl, KCl, $CaCl_2$, $MgCl_2$, Na_2SO_4). The same modeling approach is used, as mentioned above, with three adjustable parameters for every ternary gas-solvent-salt system, which are fitted to an extensive T/P/concentration range. As such the results are correlations for the ternary systems but predictions for mixed salt or mixed gas (air) solubilities. The performance of e-CPA is very good for correlation in all cases (3-12% deviation) and the salting-out effects are well-represented. The model has been applied to several mixed salt systems (with 2-4 mixed salts) and mixed gas (air) systems; in total 8 such multi-salt systems have been considered in these two studies. In these cases there are no new adjustable parameters (no ion-ion interactions are considered), thus these results are predictions. The predictive performance of the model is good with 4-6% deviation (but 16% for a 4-salt-CO2-water system).

Recent studies on e-CPA by Schlaikjer et al. [38,39]

The studies of Sun et al. [40-43] extended the applicability of e-CPA to complex salts and to gas solubilities but have not addressed the issues with e-CPA mentioned in section 4.5. Some of these issues have been investigated by Schlaikjer et al. [38,39,54] and the main conclusions are summarized here and how they have contributed to our further understanding.

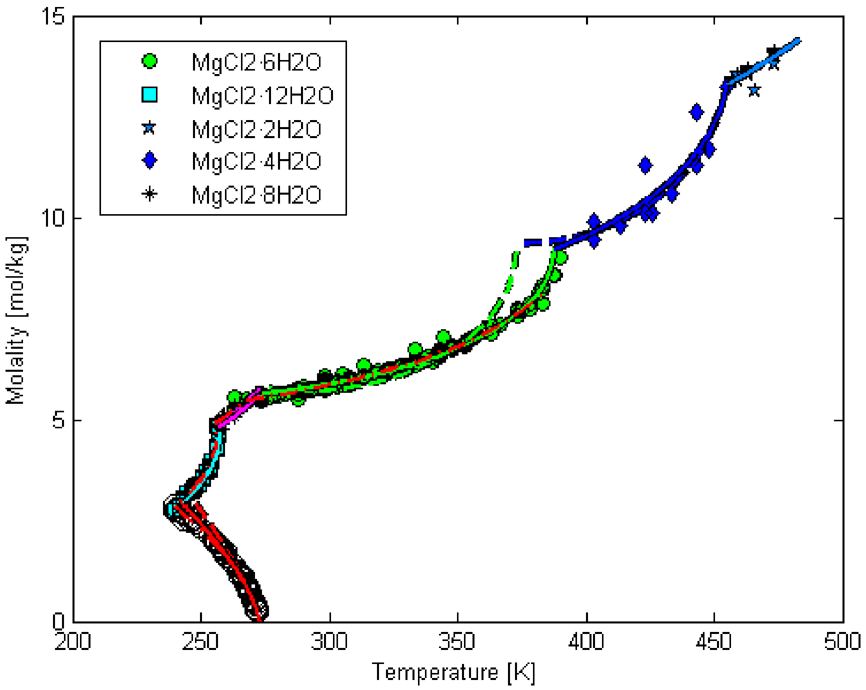
Including SLE data in the parameter estimation [38, 54]

Schlaikjer et al. [38] attempted to improve e-CPA for salt solubilities and SLE calculations. The model is essentially identical but the objective function now includes activity coefficients (mean ionic and osmotic) as well as SLE data (with the latter being weighted much more than the activity coefficients). Moreover, in addition to the three water-salt parameters (equation 7), standard state properties (Gibbs energies and enthalpies) are also fitted for almost all salts and salt hydrates. While the detailed results are presented in literature [38,54], table 6 provides a summary of the model performance and figure 1 shows representative plots. It can be concluded that it is possible to improve SLE by including such data and the standard state properties in the parameter estimation. Moreover, this is achieved without significant loss of the accuracy of the other properties (activity coefficients). From Table 6, we can also observe that the SLE performance can be improved by considering the SLE data and standard state properties in the parameter estimation after the other parameters have been fitted. But the optimum scenario is to fit all parameters (model energetic interactions and standard state properties) simultaneously as Schlaikjer et al. [38] proposed. This version of e-CPA [38] performs very similarly to extended UNIQUAC, as shown in ref. [38] and when the comparison is made in the same T-range (up to 383.15 K, which is the T-range considered for extended UNIQUAC). An observation of the values of the standard state properties of the salts and their hydrates forms from the three parameterizations shown in Table 6 (values available in references 38 and 54) show that the differences are often rather small. Still, what can be concluded is that even such small differences in the standard state property values can result to significant differences in the SLE performance and it is thus recommended to include SLE data and standard state properties of the solid salts (Gibbs and enthalpy of formation, and possibly also heat capacity) in the parameter estimation, at least when a wide range of salts is considered and very accurate results are required.

Finally, in [38] the e-CPA model performance is shown (and compared to extended UNIQUAC) as function of temperature. It can be observed that the results become progressively worse at higher temperatures and molalities (above 6 mol/kg), indirectly indicating the need for considering the ion-pairing at these conditions.

Table 6. Deviations from experimental data in form of average absolute percentage deviations using e-CPA and various modeling approaches. Adapted from references [38, 54]. The average deviations are for 12 salts. The database is shown in ref. 38 and covers extensive T/concentration ranges.

Type of property	Maribo-Mogensen et al. [20] Standard state properties and SLE not included in parameter estimation (standard state properties from extended UNIQUAC) as reported in [38]	Maribo-Mogensen et al. approach as re-parameterized by Schlaikjer [54] Standard state properties included in parameter estimation after the other parameters have been fitted	Schlaikjer et al. [38] Standard state properties and SLE included in parameter estimation All parameters incl. standard state properties are fitted simultaneously
Mean ionic activity coefficients	6.8	6.8	7.9
Osmotic coefficients	4.0	4.0	4.6
Solubility (SLE)	10.3 (9 salts)	7.1	2.9 (12 salts)



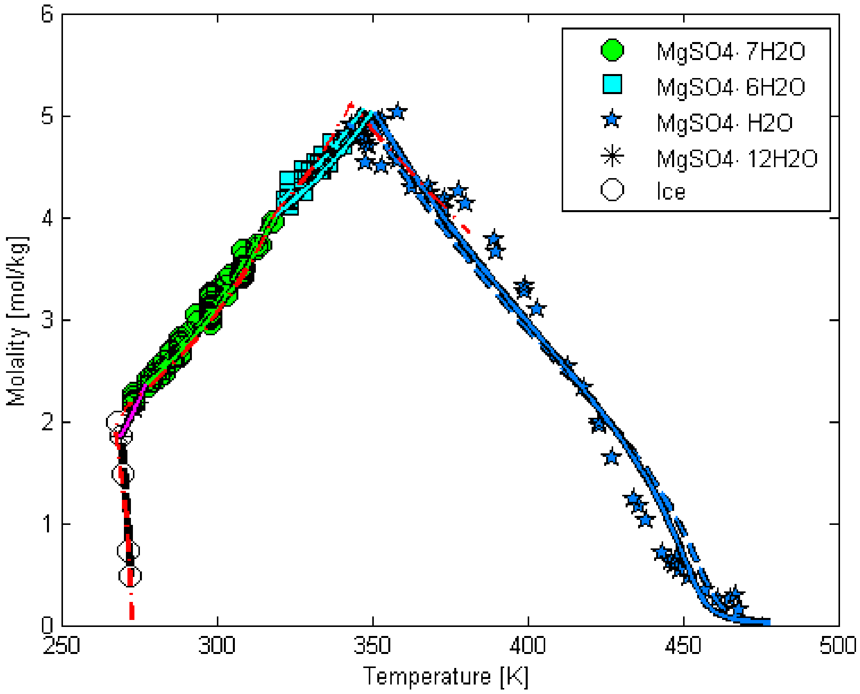


Figure 1. Solubility curves with e-CPA using (solid lines) the Schlaikjer et al. [38] parameters and (dashed lines) the Maribo-Mogensen parameters (after the standard state properties are fitted to SLE). Top figure is for $MgCl_2$ solution and bottom is for $MgSO_4$ solution. See reference [54] for information on the parameters used and references of the experimental data.

Ion-specific e-CPA development [39, 54]

Another serious deficiency of the e-CPA approach in its form from 2015 [20] was the use of salt-dependent energy parameters. Ion-specific models are to be preferred, especially for multi-salt systems, but are more difficult/time-consuming to develop. Schlaikjer et al. [39] proposed a development of the model using entirely ion-specific parameters. As estimating ion-specific parameters for a large number of electrolytes is a very demanding task, it was first important to determine the best parameter estimation approach i.e. which parameters should be fitted. 4 variations have been considered for 12 salts consisting of 7 ions in total and the results are shown in Table 7 where they are compared to the salt-specific approach from 2015 [20]. All parameters are fitted simultaneously to mean ionic and osmotic activity coefficients. The deviations are not very different between the various approaches but it is expected that the error would increase when many more salts and ions would be considered. Thus, Schlaikjer et al. [39] adopted the approach where ion-size parameters and ion-water interactions are fitted simultaneously. This approach has in total 6 ion-specific parameters for each ion (and an additional Peneloux parameter for the density). The two parameters are the ion-size and Born diameter, one parameter is the pure ion-ion interaction and the remaining three parameters are the energies between ion-water, as appearing in equation 7. These are more than twice as many parameters for each water-salt system compared to the salt-specific approach but, as Table 8a illustrates, the performance of the two approaches (ion- and salt-specific) is almost similar for the 55 salts considered, as least for the activity coefficients which are included in the parameter estimation.

For comparison purposes, in Table 8b we present a summary of results from various parameter estimation approaches with e-CPA, both salt- and ion-specific, taken from [10], where the interested reader can find all detailed results and parameters. In these approaches, different types of parameters are fitted with e-CPA for a wide range of salts/ions. Linearly T-dependency is used for the energy parameters (so in these studies, eq. 7 is not used) and occasionally, as seen in Table 8b, ion size are also fitted. Consistent with what mentioned above, ion-specific approaches require more parameters than salt-specific ones, but comparatively good performances are obtained. With the ion-specific approaches (or with salt specific ones fitting several parameters including the Huron-Vidal mixing rule volume correction, see [10] for details), it is possible to obtain satisfactory results for mean ionic and osmotic activity coefficients up to the solubility limit which can be very high. From the 50 salts considered in Table 8b, 15 have solubility limit above 6 mol/kg and 11 salts have even higher solubility limit (above 10 mol/kg).

Returning to the work of Schlaikjer et al. [38], no SLE data have been used in the ion-specific parameter estimation (unlike what was the case in the previous study, [38]). Using the same set of ion-specific parameters, Schlaikjer et al. [39] show that e-CPA provides acceptable (but not very good) densities (even with the use of Peneloux parameter), satisfactory SLE for a few systems studied and some good results for several (multi-salt and multi-solvent) multicomponent systems. More specifically, a 4% deviation is obtained on average for the osmotic coefficients of 13 mixed salt systems. Also very good description of mixed solvent (water-methanol) salt systems is shown for 4 salts. However, for these mixed solvent systems additional parameters are needed. A salt-specific methanol-salt parameter fitted to the ternary data (one parameter for each system). A typical result for a mixed solvent-salt VLE is shown in figure 2, where the data and calculations for the salt-free system are also shown.

Finally, one particular system of ions of interest is seawater or brines and the e-CPA EoS with ion-specific parameters has been applied to such a system. Figure 3 shows results for such a system. It can be seen that the prediction at 298.15 K is accurate, but the prediction at higher temperatures is less satisfactory. Still, qualitatively the correct trends are observed as the osmotic coefficient decreases with temperature, however, increasing underestimation is also observed with temperature. Thus the deviation at 473.15K is much higher than at the low temperatures. The most dominating ions in a brine solution are Na+ and Cl- as the majority of the ions in the solution are these two. Thus, as expected, the results shown in figure 3 follow the trends with respect to temperature observed for e-CPA for the water-NaCl system.

Table 7. Overview of various approaches used in the development of an ion-specific e-CPA, adapted from [54] where information on the parameters used and references of the experimental data are provided as well as detailed results for all salts. Average percentage deviations shown for mean ionic and osmotic coefficients for 12 salts with 7 ions (3 cations, 4 anions) fitted simultaneously.

Method indicating which parameters are fitted (in parenthesis the number of adjustable parameter per ion are reported)	Mean ionic activity coefficients	Osmotic coefficients
Maribo-Mogensen et al. [20] Salt-specific parameters	5.7	2.9
Only ion-water interaction (1/ion)	8.0	5.9
Ion-water interaction and ion-ion energy (2/ion)	4.4	3.4
Ion-water interaction and ion size (2/ion)	4.4	3.7
Ion-water interaction, ion-ion energy and ion size (3/ion)	3.8	3.2

Table 8a. Comparison of e-CPA results in salt-specific [20] and ion-specific versions [39]. Average percentage deviations shown for mean ionic and osmotic coefficients for 55 salts with 17 ions (10 cations, 7 anions) fitted simultaneously in both versions. Mean ionic and osmotic coefficients are used in parameter estimation in the range 273-500 K and up to 6 mol/kg. Results adapted from [54] and [39] where information on the parameters used and references of the experimental data are provided as well as detailed results for all salts.

Method indicating which parameters are fitted	Mean ionic activity coefficients	Osmotic coefficients
Maribo-Mogensen et al. [20] Salt-specific parameters	4.8	3.1
Ion-specific [39] 6 ion-specific parameters (2 size + 4 energy) + Peneloux	5.9	4.2
Ion-specific [39] 6 ion-specific parameters (2 size + 4 energy) + Peneloux + kij for some of the systems	5.1	3.7

Table 8b. Comparison of e-CPA results in salt-specific and ion-specific versions. The average percentage deviations shown for mean ionic, osmotic coefficients and apparent molar volumes for 50 salts are adapted from Bjørn Maribo Mogensen's PhD Thesis [10] and have not been previously published. In Ref. [10] are found both detailed results and the corresponding parameters for all salts as well as references to all experimental data used. The results are compared also with literature parameters and results from e-CPA, ref [20].

Method indicating which parameters are fitted	Mean ionic activity coefficients	Osmotic coefficients	Apparent molar volumes
Maribo-Mogensen et al. [20] Three Salt-specific parameters+Peneloux 54 salts-extensive T-range **Total parameters per salt: 4**	5.3	3.1	1.2
One salt specific parameter at 25 C + Peneloux Predicted ion-size parameters 0-6 mol/kg is the range **Total parameters per salt: 2**	3.6	2.5	5.3
Two salt specific parameters at 25 C + Peneloux (the one parameter is correction to Huron-Vidal mixing rule) Predicted ion-size parameters Deviations up to solubility limit **Total parameters per salt: 3**	4.3	2.3	2.1
Two Ion-specific parameters + Peneloux (the one parameter is correction to Huron-Vidal mixing rule)	6.2	5.1	

-Predicted ion-size parameters - 16 ions - 0-6 mol/kg **Total parameters per ion: 3**			
Three Ion-specific parameters + Peneloux (the one parameter is correction to Huron-Vidal mixing rule) -Predicted ion-size parameters -Linear dependency of interaction parameters - 16 ions - Results in the 0-6 mol/kg range -240-473 K range **Total parameters per ion: 4**	6.01	3.7	
Three ion-specific parameters (energy parameter, ion size, correction to Huron-Vidal) + Peneloux - 16 ions -results up to solubility limit **Total parameters per ion: 4**	4.4	2.8	5.9
Four ion-specific parameters (linearly T-dependent energies, ion size, correction to Huron-Vidal) + Peneloux -16 ions -results up to solubility limit **Total parameters per ion: 5**	4.9	4.1	

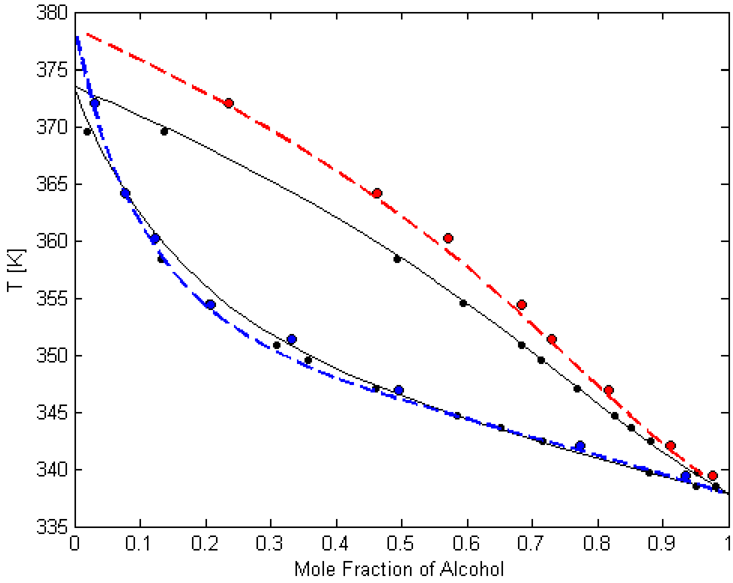
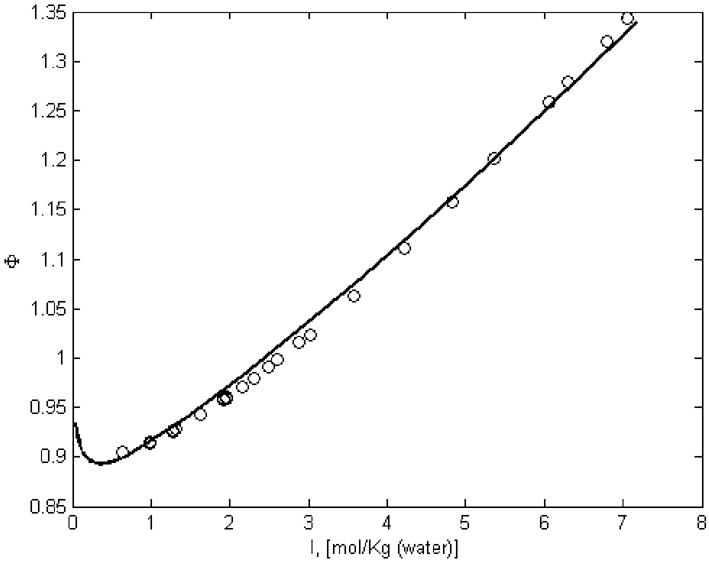


Figure 2. VLE of Water - Methanol – LiCl (4 mol/kg) with e-CPA using ion-specific parameters except for methanol-LiCl (interaction value equal to 608 fitted to ternary data). The results are shown at constant pressure of 101324 Pa. Black lines and dots are the salt-free system with CPA. The mole fraction of methanol is the salt-free mole fraction and the molalities listed are with respect to water, not the mixed solvent . From [54] where information on the parameters used and references of the experimental data are provided.



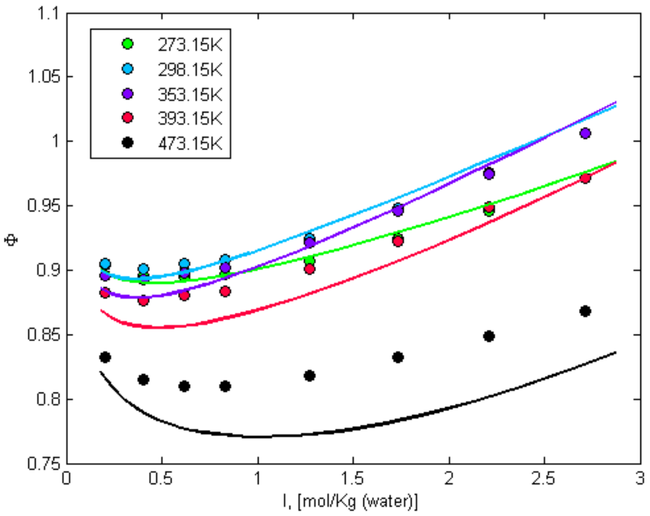


Figure 3. Osmotic coefficient of a seawater/brine solution with a specific ion composition (in moles 0.4822 Na+, 0.0553 Mg2+, 0.0105 Ca2+, 0.0094 K+, 0.565 Cl- and 0.0291 $SO_4$2-). The top figure shows the osmotic coefficient at 298.15K up to an ionic strength of 7 and the bottom figure shows the osmotic coefficient at different temperatures up to 473.15K and an ionic strength of up to 2.7. From [54] where information on the parameters used and references of the experimental data are provided.

5. New results and insights on the e-CPA approach and beyond

5.1 Multicomponent systems

Some results of e-CPA for multicomponent systems (multi-salt and multi-solvent) have been presented in the previous section. A few more results are presented here, first for the osmotic coefficients and the solubility of selected mixed salt aqueous solutions. These results are shown in figures 4-8. All systems studied have a common ion, as only in this case we can use a model with salt-specific parameters for mixed salts.

Figures 4-6 present a comparison of the two parameter sets of e-CPA [from refs. 20 and 38] for the osmotic coefficients of some mixed salts. The results are very similar, irrespectively of whether SLE data have been used in parameter estimation or not. The deviations are about 0.9% for the NaCl-Na_2SO_4 system and 5.9% for NaCl-KCl, whereas for the three-salt system the parameters from [20] (no SLE data included in parameter estimation) perform a bit better (5.2% vs. 8.1%).

Figures 7 and 8 show SLE calculations for mixed salts with the two parameter sets of e-CPA. These results and others presented in [54] demonstrate that e-CPA performs rather well with either sets, although the one based on SLE data from [38] performs overall better, especially at higher temperatures. For mixed salts containing nitrates e.g. KNO_3 and $NaNO_3$, the model has problems representing accurately the SLE data with both parameter estimation procedures, although again better results are obtained with the set based on SLE data. These problems may be due to not complete dissociation of the nitrate salts.

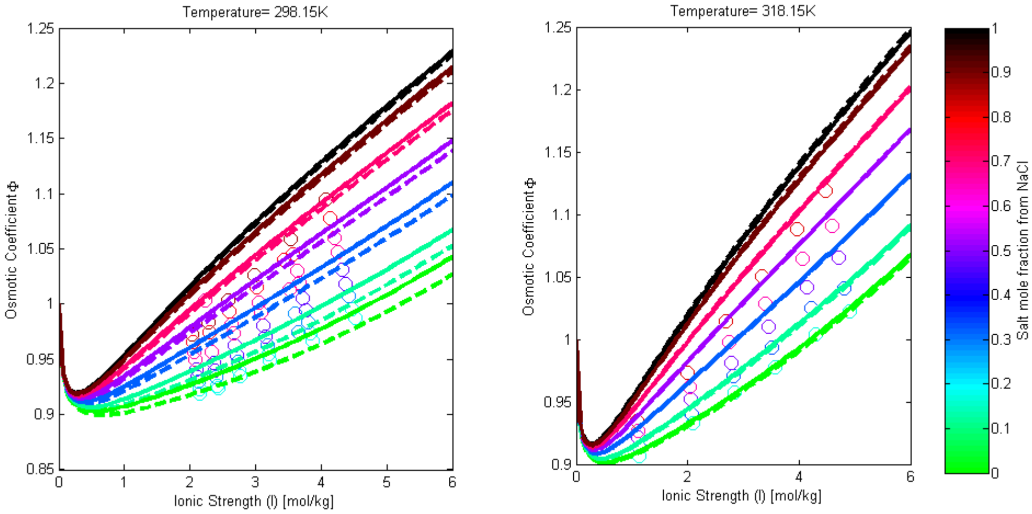


Figure 4. Osmotic coefficient of a NaCl-KCl aqueous mixture. The colorbar (various colours of the column on the right-hand side of the figure) indicate the mole fraction of NaCl in the salt mixture. Solid lines are with parameters from Schlaikjer et al. [38] and the dashed lines are with the parameters of Maribo-Mogensen et al. [20]. From [54] where information on the parameters used and references of the experimental data are provided.

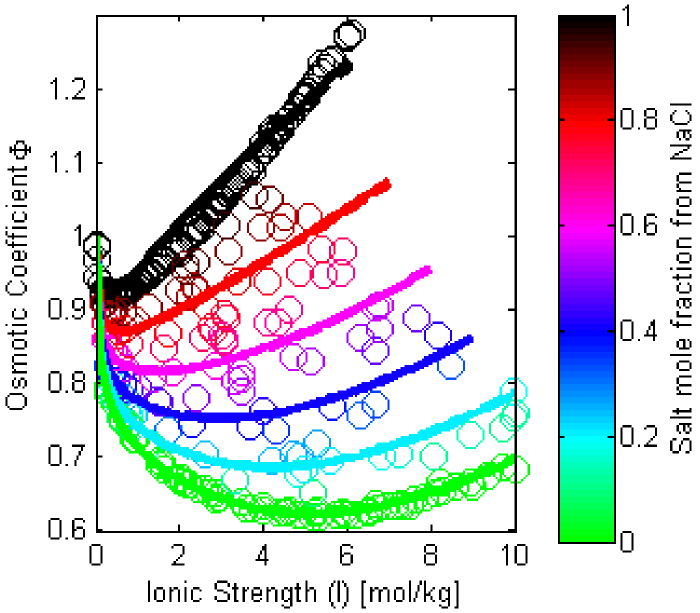


Figure 5. Osmotic coefficient of a NaCl-Na$_2$SO$_4$ aqueous mixture. The colorbar (various colours of the column on the right-hand side of the figure) indicate the mole fraction of NaCl in the salt mixture. Solid lines are with parameters from Schlaikjer et al. [38] and the dashed lines are with the parameters of Maribo-Mogensen et al. [20]. From [54] where information on the parameters used and references of the experimental data are provided.

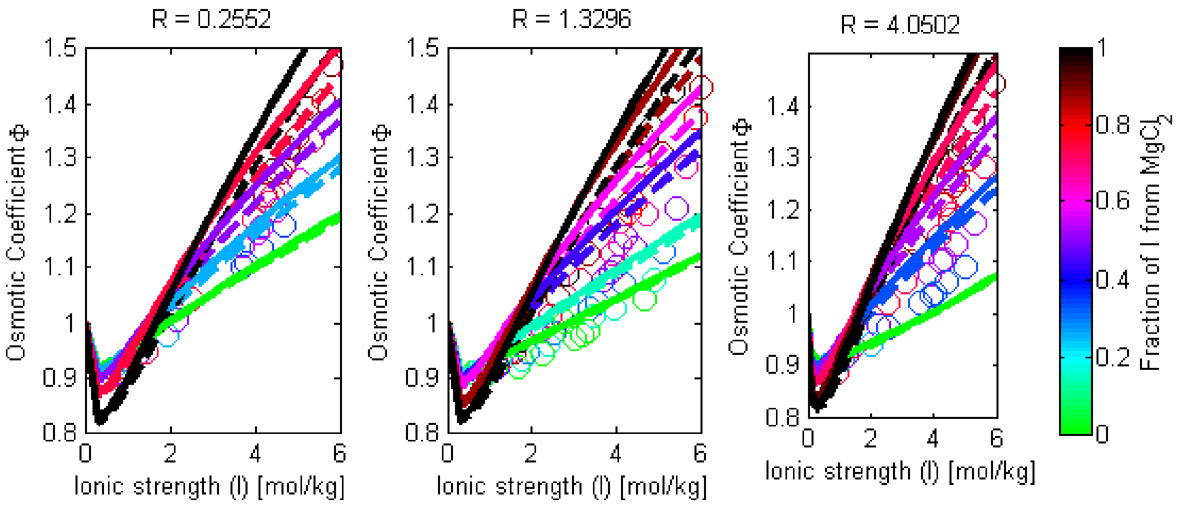


Figure 6. Osmotic coefficient of a NaCl-KCl-MgCl$_2$ aqueous mixture. R is the ratio of molality of NaCl to KCl : R = m(NaCl) / m(KCl). Solid lines are with parameters from Schlaikjer et al. [38] and the dashed lines are with the parameters of Maribo-Mogensen et al. [20]. From [54] where information on the parameters used and references of the experimental data are provided.

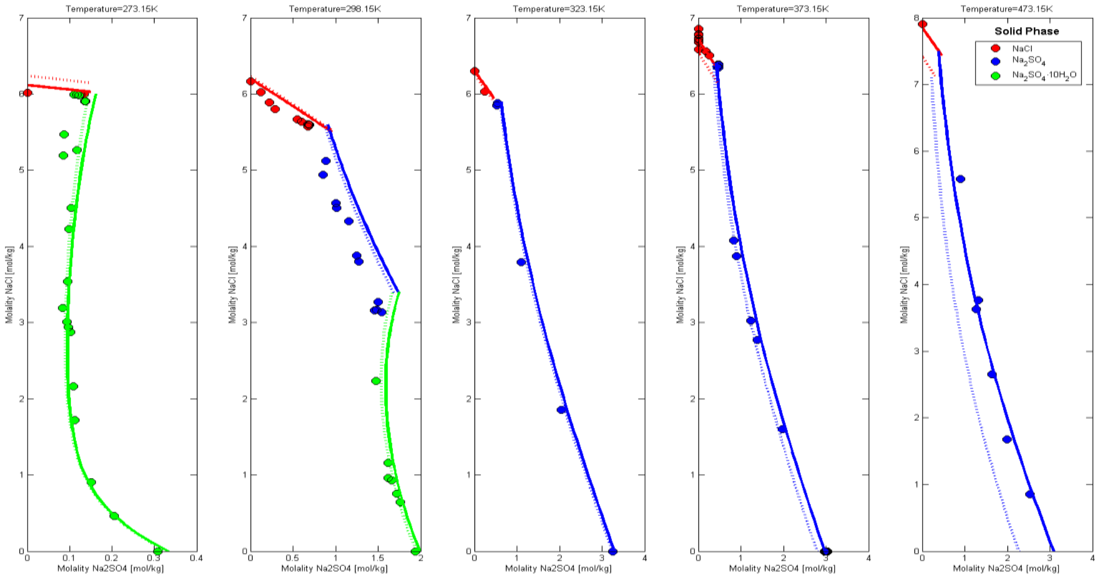


Figure 7. Solubility of NaCl and Na_2SO_4 in water at five different temperatures. Solid lines are with parameters from Schlaikjer et al. [38] and the dashed lines are with the parameters of Maribo-Mogensen et al. [20]. From [54] where information on the parameters used and references of the experimental data are provided. The solubility is shown as molality of NaCl vs. molality of Na_2SO_4 at 5 temperatures (273, 298, 323, 373 and 473 K).

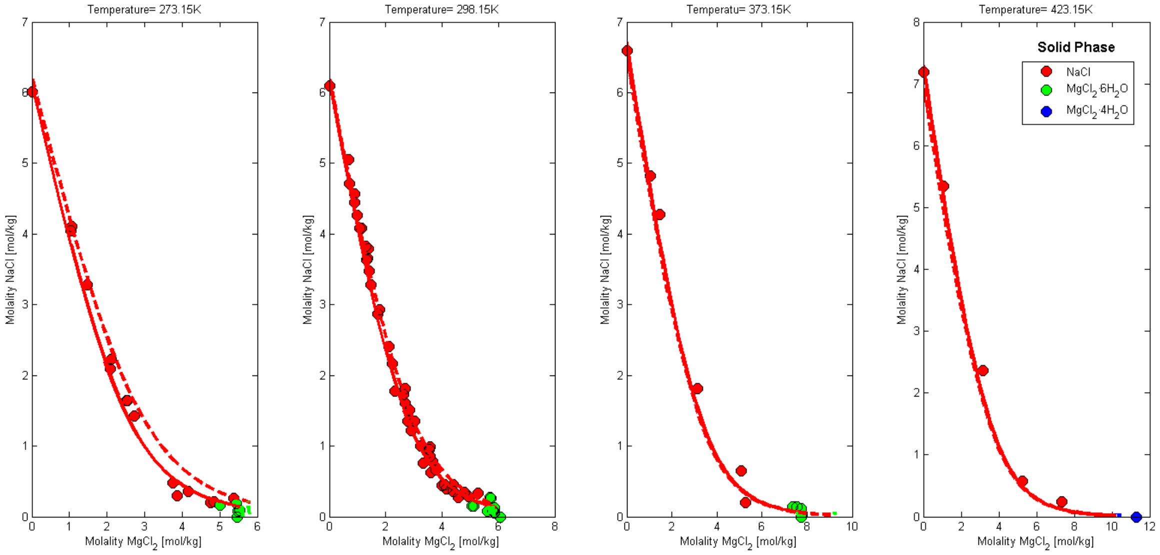
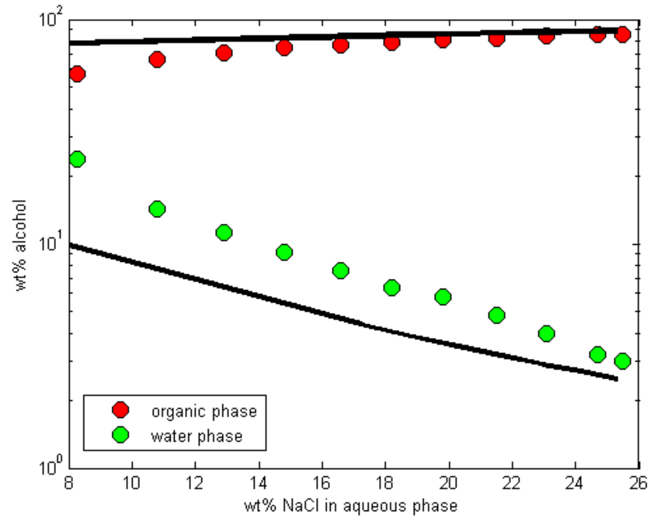


Figure 8. Solubility of NaCl and $MgCl_2$ in water at four different temperatures. Solid lines are with parameters from Schlaikjer et al. [38] and the dashed lines are with the parameters of Maribo-Mogensen et al. [20]. From [54] where information on the parameters used and references of the experimental data are provided. The solubility is shown as molality of NaCl vs. molality of $MgCl_2$ at 4 temperatures (273, 298, 373 and 423 K).

Next, we present LLE results with e-CPA for two mixed solvent systems in figures 9 and 10, in both cases using the ion-specific parameters presented in [39]. The alcohol interaction parameters with the salt are estimated to match the salts solubility in the solvent at 298.15 K.

For the water-1-propanol-NaCl system, under salt free conditions, water and 1-propanol are miscible, however, when NaCl is present it induces the liquid-liquid split. The model does capture the presence of a liquid split in the solution, as seen in figure 9. We also observe that e-CPA represents well the alcohol content in the organic phase and while it follows the trend of alcohol in the water phase, this is generally underestimated. The most serious problem is the representation of the NaCl solubility in the organic phase which is poor. The model predicts almost no salt in the organic phase. A very similar result was obtained in [20] with salt-specific parameters. A similar picture is observed for the water-1-butanol-KBr system, illustrated in figure 10. The model captures the alcohol concentration in the organic phase, while the alcohol amount in the water phase is underestimated somewhat but follows the correct trend. Moreover, where the amount of salt in the organic phase was decreasing with increasing salt in the water phase, for the water-1-propanol-NaCl system, the amount of salt in the organic phase increases with increasing amounts in the water phase for this system. This is not captured by the model, while the amount of salt in the organic phase is predicted to increase a little, especially when there is a high salt content in the water phase it does not follow the trend and is greatly underestimated.

We conclude that the main issue in the modelling LLE of these types of solutions is mainly related to the distribution of the ions in the two phases. This could indicate that the interactions between the ions and also those between the ions and the solvents do not represent correctly the actual interactions in the real electrolyte solution. Some interactions that have been left out of the eCPA in its current form are ion-ion and ion-solvent association, and adding these to the model could potentially improve the description of the LLE for these systems. Furthermore, the assumption of full dissociation is not necessarily valid in the organic solvents that have a smaller dielectric constant than water. It is clear that an accurate representation of LLE in mixed solvent calls for an improved representation of the physics of electrolyte solutions, beyond what is capable with the e-CPA versions developed so far.



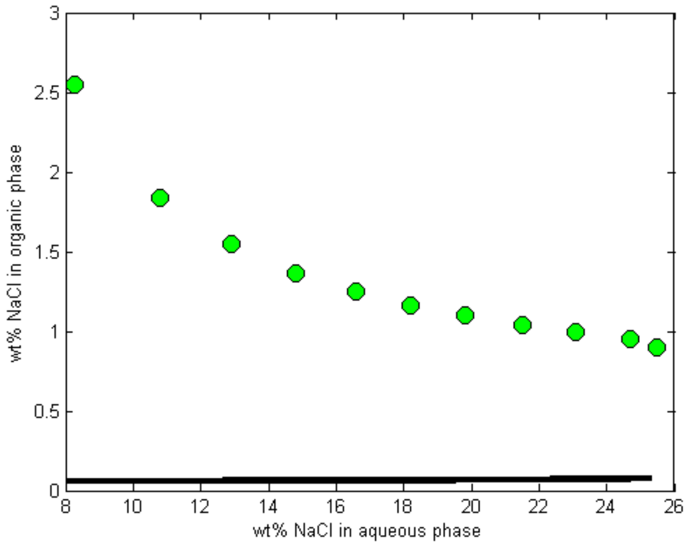


Figure 9. LLE of water - 1-propanol - NaCl at 298.15K using the 1-propanol-NaCl interaction parameter equal to 820 (estimated from the ternary data). The top plot shows the alcohol in the two phases and the bottom plot shows the salt in the organic phase. From [54] where information on the parameters used and references of the experimental data are provided.

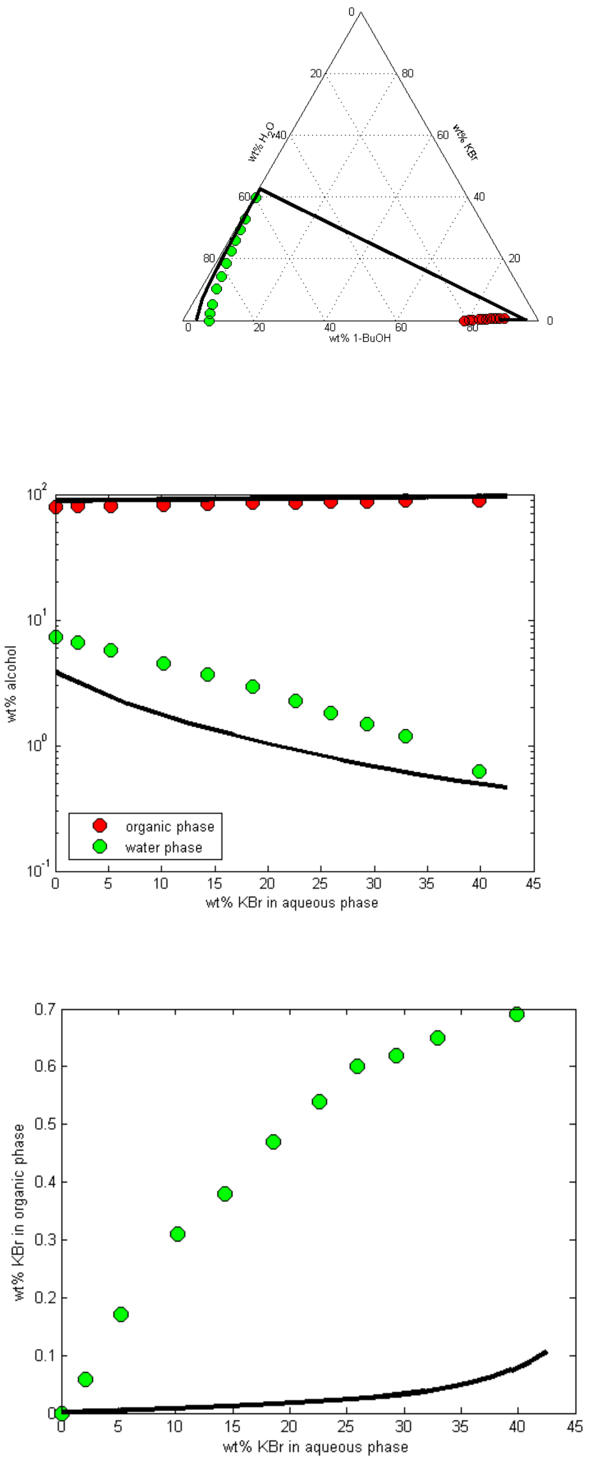


Figure 10. LLE of water - 1-Butanol - KBr at 298.15K using the 1-Butanol-KBr interaction parameter equal to 768 (estimated from the ternary data). The top plot shows the triangle diagram, the middle plot shows the alcohol in the two phases and the bottom plot shows the salt in the organic phase. From [54] where information on the parameters used and references of the experimental data are provided.

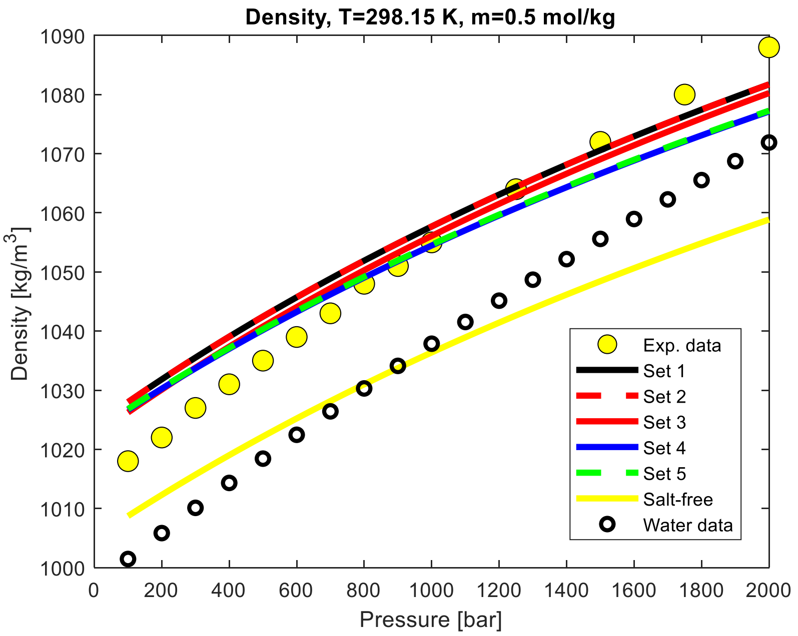
5.2 Using density in the parameter estimation

All the studies with e-CPA by Maribo-Mogensen et al. [20] and by Schlaikjer et al. [38,39] have a common characteristic that density data are not included in parameter estimation. Only when all parameters are fitted to activity coefficients (and also SLE in ref. 38), the density is “corrected” using an external temperature-independent translation parameter. This is a rather “artificial” way of representing density data and indeed as shown in ref. 39 and also recently by Due Olsen et al. [55] the representation of density of NaCl-water progressively becomes worse at higher molalities and temperatures.

In a recent study by Due Olsen et al. [55], focusing only on NaCl-water, parameters are fitted to activity coefficients (mean ionic and osmotic) as well as density data. Using the same number of adjustable parameters (salt-specific for the energies) as in previous sets, it has been shown that all properties (activity coefficients, SLE, CO_2 solubilities and densities) are represented as well or even better (e.g. the gas solubilities) compared to previous sets. In ref. [55] is also reported that densities are now much better represented at higher temperatures and molalities and we also show here, in figure 11, that the new approach (with densities included in the parameter estimation) yields also much better densities at high pressures as well (compare sets 4 and 5 to previous sets 1-3 based on translation).

When, e.g. with set 4, the density is represented correctly with e-CPA, the relative permittivity with the model presented in ref. [51] is almost that of pure water irrespectively of concentration. In this way, the Born term does not contribute to activity coefficients but still good results are obtained for the activity coefficients. In this case, it is the physical (SRK) term, which counter-balances the strong negative contributions from the Debye-Hückel term.

Finally, using set 4 (but also sets 1-3), the individual ion activity coefficients of NaCl-water are not represented well not even qualitatively so. The correct trend is obtained (set 5) only if such individual ion activity coefficient data are included in the parameter estimation. The performance for the other properties is not deteriorated with set 5, but the ion-size parameters are “unusual” (higher co-volume for cation than for the anion with set 5; we would have expected the opposite, as is indeed the case with all the other sets 1-4 investigated in ref. 55).


Density, T=298.15 K, m=0.5 mol/kg
Density [kg/m^3]
Pressure [bar]
1090
1080
1070
1060
1050
1040
1030
1020
1010
1000
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Exp. data
Set 1
Set 2
Set 3
Set 4
Set 5
Salt-free
Water data

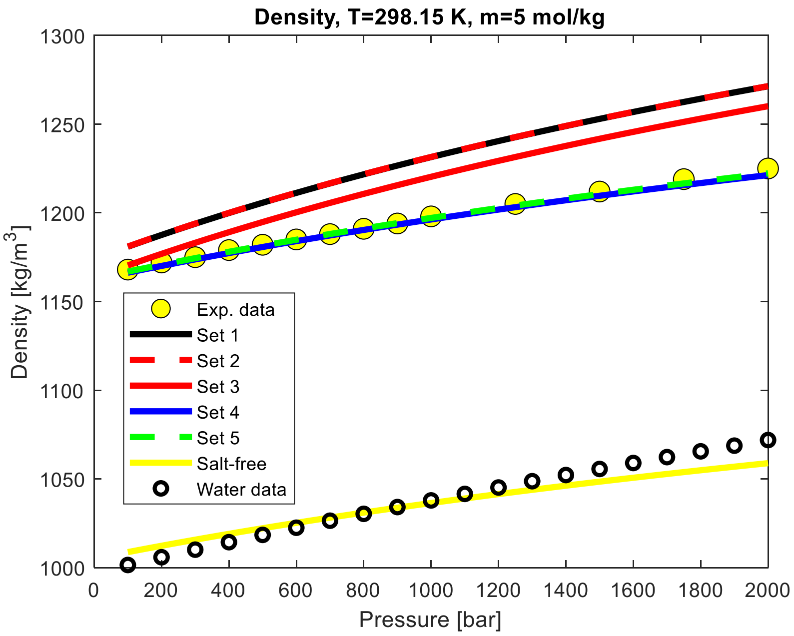


Figure 11. Density of NaCl-water at 298.15 K and two molalities vs. pressure using the e-CPA model and the five parameter sets investigated by Due Olsen et al. [55]. Sets 1-3 are the sets discussed before [20,38,39] all using the translation in e-CPA to correct for the density, while sets 4 and 5 are e-CPA parameters fitted to density in [55] as well as to mean ionic and osmotic activity coefficients. The experimental data for NaCl-water densities are from R.W. Potter II and D.L.Brown, 1977 "The volumetric properties of aqueous sodium chloride solutions from 0 to 500 C at pressures up to 2000 Bars based on a regression of available data in te literature" (Geological Survey Bulletin 1421-C).

The work of Due Olsen et al. [55] focuses on NaCl-water and it can serve as an opportunity to make a systematic parametric analysis of the role of density in parameter estimation and the importance of fitting also the ion-size parameters. Such an analysis is shown in Table 9. Three choices of "experimental" ion-size parameters and two choices of methods of estimating the co-volume parameter are used. All comparisons shown in Table 9 are made "on equal basis" i.e. with three fitted parameters in the energy term of e-CPA, eq. (7). In Table 9 are also shown for comparison the results from previous e-CPA studies [20,38,55]. Interestingly, when experimental values for ion-size are used, the best choice is with Pauling values and the 1/6 expression for the co-volume. The best set is highlighted in Table 9. Actually, in such a predictive scheme for the ion-size parameters, the 2/3 version of the co-volume fails for density (the results are as poor as literature sets in ref. 20 and 38 when Peneloux correction is not used). The 2/3 version of the co-volume parameter yields much higher values for the co-volumes compared to the 1/3 version. The best set in Table 9 (predictive ion-size parameter) performs acceptably, still with a bit higher error than Due Olsen et al.'s best set [55], which is based also on fitting ion-size parameters.

The Pauling diameters for Na+ and Cl- are (in Å) 1.9 and 3.62, while when fitted together with the rest of the parameters (set 4 in ref. 55) they become 2.38 and 3.49 Å, respectively. The Marcus "experimental values" for Na+ and Cl- used in references [20] and [38] i.e. previous studies with e-CPA are 2.36 and 3.19 Å, respectively. It is interesting to note that the ratio of Cl- to Na+ ion-size diameters is 1.35 both from Marcus values and the ones from Due Olsen et al., even though the actual sizes of ions from these two methods are different (Pauling values ratio is 1.86 for these two ions).

We conclude that there are similarities between "experimental" and fitted ion-size diameters in the case of NaCl but there are also small differences which somewhat affect the results. Whereas the performances of e-CPA for density and activity coefficient are connected, the results also show that there is "promise" in using especially the Pauling values in e-CPA as a predictive way to obtain the ion-size diameter, and only fit the energy parameters. A suitable choice of the co-volume should be used which corresponds to the ion molecular volume and the density should be included in the parameter estimation. Despite these promising results, it is early to arrive to definite conclusions whether ion-size parameters can be eliminated from the parameter estimation approach.

We will discuss ion-size parameter, link to density and parameter estimation also in the context of other e-EoS later in this review.

Table 9. A sensitivity analysis of the parameterization of e-CPA for NaCl-water in the form presented by Due-Olsen et al. [55]. Only the energy parameters of eq. (7) are fitted simultaneously to mean ionic activity coefficients (MIAC), osmotic coefficients and density. Three different choices are used for the ion-size diameter in the DH term (Pauling, Marcus and Shannon) and for each choice the co-volume parameter is estimated as:

1/6: $b = \frac{1}{6}\pi\sigma^3$

2/3: $b = \frac{2}{3}\pi\sigma^3$

For comparison purposes, the % deviations with the optimum set (set 4) shown by Due Olsen et al. [55] are 1.95, 1.62, 0.58 (MIAC, osmotic, density), those by Maribo-Mogensen et al. [20]: 2.3, 1.6, 13.3 (no Peneloux) and by Schlaijker et al [38]: 3, 1.45, 13.35 (no Peneloux), respectively.

The Born radii are the same in all cases in this comparison, and are set at 1.665 Å and 1.828 Å for Na+ and Cl- respectively. The values are from [Maribo Mogensen et al. ref. 20], and they are fitted to enthalpy of hydration data.

		Parameters			Deviations [%]		
Ion-Diameter	Ion co-volume	Uref/R [K]	T_α [K]	α [K]	MIAC	Osmotic coefficient	Density
Pauling	**1/6**	**-1186.2**	**393.1**	**6985.7**	**3.12**	**1.60**	**0.658**
Pauling	2/3	-190.7	380.5	532.4	4.28	2.54	15.59
Marcus	1/6	-1419.9	375.8	6541.1	6.06	1.53	1.46
Marcus	2/3	-225.3	415.7	578.5	4.31	2.56	12.98
Shannon	1/6	-1334.7	376.7	9346.9	3.91	1.43	1.18
Shannon	2/3	-210.6	398.6	564.9	4.30	2.55	13.85

5.3 Beyond e-cubics and e-CPA – other electrolyte Equations of State

As mentioned, this review focuses on electrolyte versions of cubic and CPA-type equations of state. There is, however, a much broader range of electrolyte EoS, many based on SAFT and it is worth including some of most characteristic ones in this presentation, facilitating also the general discussion in the next section. It can also be speculated that for electrolyte solutions, the choice of the "physical" term of model (cubic, CPA, SAFT) may be less important compared to how the electrolyte interactions are accounted for and the parameter estimation approach followed.

As by now numerous electrolyte EoS have been proposed, we will briefly present in this discussion only some of them, from major research groups who have worked on the electrolyte EoS areas for many years. In particular, we will mostly discuss the e-PC-SAFT approaches by Jean-Charles de Hemptinne and co-workers ("IFPEn group"), the e-PC-SAFT by Gabriele Sadowski, Christoph Held and co-workers ("Dortmund group"), various e-SAFT approaches by Amparo Galindo, George Jackson and co-workers ("Imperial group") and finally also diverse e-EoS approaches by Ioannis Economou, Marcelo Castier and co-workers ("Texas A&M group"). The objective function used in these models and fitted parameters are summarized in Table 10, where the e-CPA approaches are also presented for comparison purposes.

Table 10. Overview of models and parameter estimation methods

MIAC = mean ionic activity coefficients; AMV = apparent molar volumes; Dens = density (ρ); Osm = osmotic coefficients = Φ; SLE = solid-liquid equilibria data (salt solubilities)

Group	Model	Year/References	Objective Function	Parameters fitted (per ion/salt)	Comments
Prausnitz	e-cubic	1991, 13	MIAC, ion chemical potential	Size of ions + kij of ion-water	Few systems
Sandler	e-cubic	2002, 17	MIAC, osmotic, density, Gibbs energy of solvation	Energy, co-volume, size of salts + kij (water-salt)	Many parameters are heavily T-dependent
Renon	e-cubic	1993, 15	Osmotic	Sizes of cations, anions and energies of cation-anion and cation-water	All model parameters are functions of parameters for diverse ions 6 parameters for 16 ions
Prausnitz	e-CPA	1998, 16	MIAC, water activities	co-volume and energy of ions	Only NaCl-water-methane
IFPEn	e-CPA	2008, 18	MIAC, AMV, Osmotic	Energy of ions, kij (ion-water), Born diameter	Pauling data for MSA diameter
DTU	e-CPA (and other models)	2007, 19	MIAC, Osmotic, AMV, SLE	Energy, co-volume and diameter of ions and kij for ion-weter	
	eCPA	1995, 20	MIAC, Osmotic	3 salt-water energy parameters	+extra Peneloux for density Ion sizes from literature
	e-CPA	1997, 38	MIAC, Osmotic, SLE	3 salt-water energy parameters + standard states	+extra Peneloux for density Ion sizes from literature

	e-CPA	1998, 39	MIAC, Osmotic	3 ion-water parameter, DH and Born sizes, pure energy parameter (6 parameters per ion)	+extra Peneloux for density
	e-CPA	2019-2021, 40-43	Water-salt-gas	Same model as reference 20 + 3 gas-salt parameters	Predictive for mixed salts
	e-CPA	2021, 55	MIAC, Osmotic, density	3 salt-water energy parameters + density	
IFPEn	e-PC-SAFT (polar)	2013, 56	MIAC, AMV	Ion-water association parameter	Ion diameter from Pauling
	e-PC-SAFT (polar)	2018, 57	MIAC, AMV	Ion-water association parameter and ion-diameter	
Imperial	SAFT-VRE	1993-2003, 68,69	Vapor pressure	Ion-water dispersion parameter	Ion diameter from Pauling
	SAFT-VRE	2014, 70	MIAC, vapor pressure, density	-Ion-water dispersion parameter - ion-ion energy parameter - ion diameter	3 parameters per ion
	eSAFT-VR Mie	2016, 71	Vapor pressure, density, Osmotic	Ion-water dispersion parameter	-All other ion energies and diameters from theory -MIAC are predictions -2 ions considered associating
Texas A&M	eSAFT-VR Mie	2018, 72	MIAC, density	Ion size and ion-water	-2 parameter per ion (T-

				interactions	independent)
	Q-electrolattice	2013, 75	Vapor pressure, MIAC	Energies of ion-solvent or salt-solvent	Diameters from Marcus
		2014, 76	MIAC, density	Ion size,ion-solvent energies	
Dortmund	ePC-SAFT	2005, 60	Vapor pressure, density	Ion size and ion-water interactions	
	e-PC-SAFT	2008, 61	MIAC, density	Ion size and ion-water interactions	Vs. ref. 60 – vapor pressure based parameters not good for MIAC
	e-PC-SAFT (revised)	2014, 63	Osmotic, density	Ion size and ion-water interactions, kij (ion-water), kij (ion-ion)	
	e-PC-SAFT (advanced)	2021, 65,67a	----	Transferable parameters from e-PC-SAFT revised	
	e-PC-SAFT (advanced)+ Bjerrum	2021,66,57b	----	Transferable parameters from e-PC-SAFT revised	
Shahriari-Dehghani	ePC-SAFT	2017, 59	MIAC, AMV	Ion size and dispersion energy Association energy of ions	-Association volume of ions is constant, same for all ions -3 parameters per ion
	SAFT-VR Morse	2018, 87	MIAC, density	Ion size and dispersion energy Length of potential for ion, k(ion-water)	

IFPEn group

From the IFPEn group, the e-PC-SAFT with an additional polar term has been used/developed in several studies [56,57]. In both cases the MSA theory is used for ion-ion interactions and a Born term with a composition-dependent relative permittivity is also added.

In [56] the short-range (SR) water-ion interactions are accounted for via sites for ions with the water-ion association energy being adjusted. Successful results are presented for activity coefficients, up to molality of 6 mol/kg, and densities, but there are problems at higher temperatures without T-dependent parameters. No SLE results are shown. The density has not been fitted to experimental data and this may be the reason for the not so accurate densities obtained. In some sense the work of Rozmus et al. [56] is rather "bold" in the sense that "experimental" (Pauling values) are used for ion-size parameters and the same values are used in MSA, Born and physical terms. Clearly the target of the IFPEn group was to have as few parameters as possible, as only energy parameters are fitted to experimental data, which are T-independent. However, this simplicity has the consequence of an error of about 5% in density which is much larger than what Held et al. [63] report for PC-SAFT (about 0.5%), see discussion later, where also ion-size parameters are fitted to density (and other) data. Even though the parameters by Held et al. are not very different from Pauling's parameters, the sensitivity of the results especially for density to the actual values of the ion-size parameters is great.

Ion-pairing is discussed and these researchers believe that without such considerations, poor activity coefficient results should be expected at high temperatures and molalities above three. As implied in their model, they attempt to account for ion pairs via ion-ion association using the Wertheim theory instead of considering dispersion interactions. 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. Despite this accounting of ion-pairing, problems still prevail at high temperatures and even higher molalities.

Nevertheless, Rozmus et al. [56] discuss the difficulties associated with assigning sites to ions. It may be expected that such association sites should be related to the hydration numbers of ions but only rough correspondences exist, as shown in [56]. Hydration numbers are typically 4-6 for the more hydrated cations and lower for the anions, but as shown in [56] the association site values range between 6-8, with cations around 7-8 and somewhat lower for anions. An interesting observation in [56], using their e-PC-SAFT, is that with increasing ion concentration, hydrogen bonding decreases, thus observing a disruption in water structure, something observed by other researchers as well [58].

Finally, as was the case also with their e-CPA [18], the IFPEn group observes [56,57] that, when a composition dependent relative permittivity is used, the magnitude of the Born term is as significant as of the electrostatic interaction (from MSA) and can, thus, not be ignored. This conclusion is in agreement to the e-EoS of Simon et al. [13] but also more recently with the results shown by Shahriari and Dehghani [59]. These researchers, [59], also presented an e-PC-SAFT, with Born, but using the full Debye-Hückel instead of MSA. The conclusion on the relative magnitude of Born and ion-ion terms remains the same (equally large and opposite contributions). Their model [59] has similarities to the work of the IFPEn group [56] in terms of including a Born with composition dependent relative permittivity and assigning sites to ions (6 for cations and 5 for anions). They present very good results for many properties (activity coefficients, density, SLE, solvation energies, heat capacities) but at rather narrow molality range (max 6 mol/kg). They consider that including the Born term is important also for the representation of derivative properties.

The more recent work from the IFPEn group by Ahmed et al. [57] extended the e-PC-SAFT to mixed-solvent salt VLE (but no LLE is shown) and salting out for several gases. Unlike the previous work of the group, now both ion diameters and ion association energies are fitted to mean ionic activity coefficients and apparent molar volumes with good results at room temperature. The fitted ion diameters are used in the MSA term, while the Pauling values are used in the physical term of the model (assuming that the diameter in the physical term is the “bare ion”) as well as in the Born term. Indirectly, the authors consider that the MSA diameter describes the ‘solvated’ diameter, i.e. ion + surrounding water. An improved parameterization of water is also included in this model. In [57] the global average deviations in MIAC and AMV are 3.9% and 24% compared to 3.9% and 30%, respectively with the same model from the previous work of the authors [56].

Although no detailed comparisons with other models from literature (from other groups) are provided in the paper [57] the performance of the model, compared to the previous work of the group, for density has been improved now that ion-size parameters are fitted (also) to density data. The authors present results for apparent molar volumes, which are more sensitive than solution densities alone. The mixed solvent electrolyte VLE results shown are satisfactory and predictions (all parameters previously obtained, no ternary data used in the parameter estimation). For the salting-out curves, however, a gas-ion correction parameter for the cross-diameter is obtained directly from the ternary water-salt-gas data. Thus, these results are correlations and of some interpretative value.

A term analysis is also shown in [57] with, in agreement to previous studies, illustrate that Born and MSA (ion-ion) terms have large opposite contributions to the activity coefficient. A concentration-dependent dielectric constant was used in both terms. Interestingly enough, this well-established (for several salts and models) balance of terms is not followed by fluorides, whose behavior is dominated by association.

Dortmund group

We now return to the Dortmund group who has also proposed an electrolyte version of PC-SAFT, originally [60-63] without the Born term, but recently [64-67], a Born term was included with a composition dependent relative permittivity. The e-PC-SAFT of Dortmund uses the full Debye-Hückel equation for the ion-ion interactions. Using fitted ion segment energies and ionic (”hydrated”) diameters to mean ionic activity coefficients and densities, good results are obtained for these two properties for over 100 single salt-water systems and up to very high concentrations (0.8% deviation for densities, 3.3% for VLE and about 9% for mean ionic activity coefficients). In their version, the association term of PC-SAFT is used only for water, which is, somewhat surprisingly, assumed to have only two association sites (2B scheme) with a 4-parameter temperature dependency is used for the segment diameter of water in order to ensure excellent representation of vapor pressures and liquid densities. No high pressure density results were shown.

The results with Dortmund’s e-PC-SAFT version have several good qualitative features as well, e.g. good description of the reversed mean ionic activity coefficients series for alkali hydroxides and fluorides, physically meaningful values for the ion diameters (close to experimental hydrated diameter values, see discussion later) and ion dispersion energies e.g. when presented for various salt families or ion series as well as physically correct trends of mean ionic activity coefficients e.g. smallest alkali cations yield higher activity coefficients due to the stronger hydration.

The Dortmund group has not tried to represent the activity coefficients and densities only with a single parameter fitted (energy). They are of the opinion that, using the energy parameter alone, it is possible to adjust the slope of the MIAC at higher molality, while with the diameter it is possible to additionally shift the minimum of the MIAC. It appears that, as is the case with other SAFT models, this activity coefficient minimum is not 100% perfectly matched, and due to this reason, fitting also to density is important. Only fitting to MIAC definitely leads to poor densities is the authors’ view, which appears to be correct.

However, it should be mentioned that, possibly due to the interest of the Dortmund group for biological applications (amino acids, peptides, …), all results are initially reported at 25°C and no results have been shown at higher temperature or SLE. In [63] some successful results are shown for ternary activity coefficients and densities of mixed salts and mixed solvents (water-alcohols) as well as water-salt-amino acids. In [63] all the model parameters (energies and diameters) are revised to include the ion-ion dispersion interactions, not included in the earlier studies [60-62], and some results are also reported at higher temperatures for activity coefficients without additional T-dependent parameters.

As one of the few groups, ternary LLE results have been reported for a few systems (water/NH_4Cl/1-butanol) in [63] but now it was needed to include also cation-anion and ion-alcohol/water interaction parameters fitted to the ternary data. This approach “mimics” ion pairs at high salt concentrations, using solely dispersion interactions and without using extra terms. These results are only partially successful and they are not predictive. Nevertheless, this approach was considered necessary at high concentrations where ion pairs may exist and for weak electrolytes. The LLE for water-salt-hydrocarbons and water-salt-1-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.

Recently, the Dortmund group has extended the e-PC-SAFT approach by adding a Born term in the model, also with a concentration dependent relative permittivity [64-67]. They used the same ion-water parameters (from their 2014 revision, ref. 63) and the same ion-size parameters (which were fitted to water systems) also for non-aqueous and mixed solvents. They have called the new model “e-PC-SAFT advanced”. In one of the studies [66, 67b] a Bjerrum term for ion-pairing is also included. The authors present many successful results demonstrating the importance of using the Born term with a concentration-dependent dielectric constant particularly for non-aqueous/mixed solvent systems. The results presented are impressive both because many ion-size and interaction parameters are transferred from aqueous systems and because the ion-solvent interactions are set to zero. Thus, the results e.g. for activity coefficients of salts in alcohols shown by these authors can be considered to be predictions. Successful results are obtained only when the Born term and composition dependent dielectric constant are included in the model. The Born term is also very important for the Gibbs energy of hydration, but less so for the Gibbs energy of transfer for ions from water to alcohols. The authors also show, in agreement to other studies, that Born and Debye-Hückel terms have large opposite contributions to the activity coefficient.

In two of the studies [66, 67b] the role and importance of ion-pairing are demonstrated and a review of models accounting of ion-pairing and/or applied to water-poor systems is presented. Some promising observations are made but it appears that the effect of the Bjerrum ion-pairing treatment is relatively small for the activity coefficients of alcohols in salt solutions, compared to including the Born term and a composition dependent dielectric constant. Still, using the Bjerrum approach reliable values for the degrees of dissociation of some salts in several organic solvents (but not in ionic liquids) can be obtained.

In one of the very recent manuscripts [67a] promising results for ternary LLE of several salt-mixed solvent systems are presented with various modeling strategies. This study shows that Born term and concentration dependent dielectric constant are very important but especially when a mass fraction mixing rule is used for the dielectric constant. The deviations shown for the LLE of 7 out of 9 ternary mixed solvent-salt systems are very satisfactory (15-30% deviation for the compositions), considering that all calculations appear to be predictions (parameters from binary data alone; ion-solvent interactions seem to be zero). The authors conclude that the Born term is crucially required to obtain the correct partitioning of a salt between an aqueous phase and an organic phase without fitting too may extra parameters (which may also obtain unphysical/high values).

Imperial group

The Imperial group has been developing electrolyte SAFT EoS for over 20 years, first [68,69] as extensions of the SAFT-VR model and more recently [70,71] also as extensions of the SAFT-VR Mie EoS. In all cases MSA is used for ion-ion interactions, while a Born term with a relative permittivity having a weak salt composition dependency is included in the recent studies [70,71]. How much the Born term, as used in the Imperial group, affects the activity coefficients is not entirely clear.

In the earlier studies [68,69] the focus was on VLE and densities for a few water-salt systems and salting-out curves (with methane), as well as gas hydrates with salts. For these rather simple cases, a single fitted ion-water dispersion parameter was sufficient and the Pauling diameters were used in the models. No alkane-ion interactions are considered in the case of systems with alkanes/gases and salts. No activity coefficients, SLE or mixed solvents were considered in these earlier investigations. The only hydrogen bonding interactions allowed are those between water molecules, which are modeled using the 4C scheme. The results for the properties considered, especially VLE and salting-out curves, are satisfactory. Even with these few adjustable parameters, SAFT-VRE is shown to predict correctly the salting-out of methane from water due to NaCl and interesting conclusions are extracted on the salting-out effects for other alkanes and from various salts. There are not much experimental data for water-alkane-salt mixtures, but SAFT-VRE predicts that the compositions of the alkanes in the water phase are seen to be reduced by orders of magnitude upon salt addition.

The recent studies with SAFT-VRE and eSAFT-VR Mie [70,71] are more extensive and many properties and conditions are considered: densities, water activities, activity coefficients up to high molalities and temperatures (limited studies at high temperatures), freezing-point depression curves 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 presented over a temperature range. The VLE of mixed solvent-salt shown demonstrate good agreement with data, including the effect of salt concentration on water-methanol VLE at increasing concentration of various salts [70]. LLE for a single system (water-1-butanol-NaCl) is shown as well [70]. Both for mixed solvent VLE and LLE systems, there is a need for an alcohol-ion dispersion energy interaction, which is fitted to the ternary data. Under these conditions, the performance of the model is good, including the salting-out of alcohol in the presence of salt. It is interesting that mixed solvent VLE and LLE are not considered in the more recent eSAFT-VR Mie work by Imperial group [71], but instead some SLE calculations at room temperature are provided, with acceptable results for some salts, although several salts have solubility limits higher than the salt concentration limit where the authors state that eSAFT-VR Mie is applicable.

A particularly interesting point in the recent work of Imperial group [71] and some of the earlier ones [69,69] is that, unlike most other groups, the ion-size parameters are not fitted to experimental (density and other) data but are taken from literature, both in the earlier and more recent studies (Pauling and Shannon values). These researchers are well-aware of the importance – role of ion-size parameters with connection to getting accurate densities (and even activity coefficients) but they chose their approach as they considered that it is difficult to select unique ion-size parameters. Of course, this is done at some cost. The densities obtained in [71] have deviations of about 2-3%, much higher compared to less than 1% obtained with the same model when the ion-size parameters are fitted to density and other data [Selam et al., 72].

Of particular interest are the good results presented for the free energy of solvation (4% in [71] for 13 ions) attributed to the inclusion of the Born term with different diameters from those used in the ion-ion term (MSA). Some authors have stated that such a "primitive" approach, as all the e-EoS reviewed in this work are, should not be expected to perform very well for solvation energies but the good results obtained indicate this is not the case! Very good results for energies of solvation have been reported in other studies as well e.g. in [59] for an e-PC-SAFT+Born+DH model (6.4% deviation for 8 salts).

Unlike what was the case in the IFPEn and Dortmund groups, in the studies so far by the Imperial group including the recent ones [70,71], ion pairs and ion-water association are not considered explicitly. The authors, aware of the possible importance of ion-pairs at high concentrations, they limit their applications to lower concentrations. It is not clear, however, which is the "maximum molality" that should be used for model development and validation as different values are presented in their studies (molality equal to 10 mol/kg in ref. 70 and in ref. 71 the maximum molality is 3 mol/kg for parameter estimation and 6 mol/kg for model validation). 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.

Texas A&M group

Overall the developments with eSAFT-VR Mie have been quite interesting and there are some very promising results. The eSAFT-VR Mie project has been continued also by the Texas A&M and DTU groups, as shown in a number of publications [72-74], where now the full DH equation is used for ion-ion interactions as well as a Born term which is salt composition-independent, thus not affecting the phase equilibria. Selam et al [72] applied the eSAFT-VR Mie with two fitted parameters for each ion (ion-size and dispersion interaction with water) obtained from mean ionic activity coefficients and densities with good results at room temperature but T-dependent interaction energies are needed at higher temperatures. 18 ions have been considered permitting the representation of at least 68 salts (8 electrolyte families) for which detailed results are shown for mean ionic, osmotic activity coefficients and vapor pressures (latter properties not in parameter estimation. Inclusion of the Born term in the model permits the estimation of Gibbs energies of solvation with errors between 1% (Ca2+ and Li+) up to 26% (I-) and on average 13% for 15 ions. Activity coefficients and densities for mixed salts are well-represented in most cases. Novak et al. [73,74] have illustrated the success of the approach for water-alkane VLE and LLE (even in absence of interaction parameters) and also applied successfully eSAFT-VR Mie to a very wide range of salting-out curves for many gases and salts. Very good results are obtained with newly estimated T-dependent ion-water parameters (shown for 9 ions) and ion-gas parameters fitted to gas solubility data (efforts to predict this parameter are shown but are not very successful). Very good predictions are shown with eSAFT-VR Mie for several multi-salt solutions.

Another interesting electrolyte model from the Texas A&M group, developed prior to eSAFT-VR Mie, is the Q-electrolattice EoS [75-77] which combines the MTC EoS for the physical term with the MSA and Born contributions; in both terms is used a relative permittivity that is salt-concentration dependent. As for the eSAFT-VR Mie, Q-eEoS has ion size parameters and ion-water energies as fitted parameters based on mean ionic activity coefficients and density data. 10 ions are considered. Very good results are shown for activity coefficients (mean ionic, osmotic) as well as for vapor pressures and densities. In the 2013 work [75] the ionic diameters are "experimental" (from Marcus), but in the subsequent works [76,77] they are fitted as mentioned. This was done primarily in an effort to improve the density of water-salt systems; the link of fitted ion size parameters and improved density results is clear and the effect of salinity on density was correctly captured by the Q-electrolattice model. Once again, also these authors observed that the density results were very sensitive to the ion size parameter values used.

Concluding remarks

In summary, in terms of applications of e-EoS, as seen from literature, we observe that most studies focus on (mean ionic) activity and osmotic coefficients and densities are also often considered, but apparent molar volumes are mostly ignored. Gas solubilities are considered in several studies but only in a few studies this is done systematically. Gibbs free energy of hydration is considered by many models, satisfactorily only by the models which include a Born term. Temperature and concentration ranges differ a lot in the various studies. Among the properties which are very rarely considered are SLE and thermal properties and there are only few studies on mixed solvent VLE, and not much success in the even fewer studies on mixed solvent LLE. Finally, individual ion activity coefficients are not considered in most studies, despite that quite a few data are available. Even if some consider these data to be controversial, we believe that they can be used at least for qualitative purposes.

It is evident that comparisons of e-EoS, based alone on the study of literature, is almost impossible due to the very different parameterizations adopted and also the fact that many groups have considered different models and different development methods. There is often no discussion why one approach is preferred over the other, but we hope that this review provides some insights.

We also hope that the recently developed open-source software Clapeyron by Pierre Walker and co-workers may offer in the future possibilities of comparisons and benchmarking of e-EoS. The developers have developed and incorporated in their software generalised Electrolyte SAFT model which lets users freely switch which between SAFT, ionic, born or R.P models they want to use (so one could hypothetical do combinations of PC-SAFT+MSA+Born+R.P model by Maribo-Mogensen et al, [51,53]). Officially, the following models are included so far: SAFT-VRE Mie, ePC-SAFT and e-CPA and more are on the way. For more information, the following links can be used:

- URL: https://github.com/ypaul21/Clapeyron.jl
- DOI: 10.5281/zenodo.5508638 (Zenodo repository)

6. Discussion of the electrolyte equations of state (based on cubics, CPA and beyond)

We will now provide a unified and comparative discussion of all the electrolyte EoS models presented in this review, also as compared to some other approaches. We start this discussion with two special topics in electrolyte modeling applications, proceed with discussion of the role of ion-size dimensions and the relative significance of the EoS terms. An attempt to present "the big picture of e-EoS modeling" and our views on current status and way forward is presented in the conclusions.

6.1 Two special topics

There are many special topics in electrolyte thermodynamics, we touch up two of them here. First of all, the two different frameworks (Lewis-Randall, LR and McMillan-Mayer, MM) typically used in the development of the (primitive-based) electrolyte equation of state. The "classical" LR is used for the short-range terms e.g. cubic, CPA or SAFT, whereas the MM is used for the ion-ion interactions, irrespectively if DH or MSA are used. This happens because the solvent (typically water) is considered to be a continuous medium characterized by its dielectric constant, rather than a component. The LR framework has as independent variables *T, P*, mole numbers of all species, while the MM framework has independent variables *T, V*, mole number of solute, chemical potential of solvent. So, do we need "corrections" when two presumably different frameworks are combined in complete e-EoS and how important are these corrections? This is not an easy question to answer. Prausnitz et al. [1] state 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 (almost all), such corrections have been ignored or it is considered that they may be absorbed in the adjustable parameters (present in all models). A few researchers (Radosz and co-workers [78a-c] and Myers et al. [17]) have quantified these corrections to be very small, while others who have included them (like Wu and Prausnitz in their e-CPA, [16]) do not comment on their practical significance. According to Mollerup and Breil [79], the use of the MM framework confuses the discussion of electrolyte thermodynamics and they are not sure how useful it is. Nevertheless, the topic is not entirely clarified and corrections may be needed for systems with mixed solvents in particular, as discussed several years ago from O'Connell and co-workers [80-82].

Another important topic is the use of standard state properties needed for solid-liquid equilibrium (SLE) calculations. Such type of calculations are very important in many practical applications and actually one of the strong points of famous activity coefficient models such as extended UNIQUAC and Pitzer. It is rather surprising that among the so many e-EoS proposed, SLE calculations are presented in only few studies [20,38,39,70]. This is unfortunate as such data can permit the validation of the models over extended molality and temperature ranges. This of course brings the models “at their extremes” as high concentrations and/or high temperatures can result to problems, sometimes significant e.g. due to ion-pairing, as discussed. This is not the only problematic aspect with SLE calculations. Standard state properties (Gibbs, Enthalpy and Cp) are needed for both single and mixed (hydrated) salts. Such data are often not available, maybe sometimes they can be taken from literature e.g. from well-established activity coefficient models such as extended UNIQUAC. As discussed in this review [see also 38,39], the sensitivity of the SLE results to the values of such parameters is significant. If very accurate results are needed for SLE, both standard state properties should be included in parameter estimation simultaneously with the other parameters and SLE data should be used in parameter estimation. These are our observations [38] so far and it will be a great way forward for e-EoS if such standard state properties can be obtained from independent measurements or quantum chemical calculations while maintaining an overall good modeling performance of the e-EoS for a wide range of properties.

6.2 Ion-size parameters

Table 11 presents ion-size parameters (diameters) from diverse “experimental sources” (Pauling, Marcus, Shannon, [83-85]) and from some of the models discussed in this review. With few exceptions, these parameters are used only in the ion-ion terms of the models (MSA or DH) as the Born term typically requires “higher values” of ion-size parameters. The ion-size parameter is one of the most interesting parameters of the e-EoS models. The reason is that, being a parameter with a rather clear physical meaning, it is tempted to use “as it” i.e. taken from one of the experimental sources e.g. [83-85]. Which of the experimental sources should be used is not entirely clear. It is not also clear whether the same ion-size parameter should be used in the physical and the ion-ion interaction term of the model and different researchers have used various approaches. The values shown in Table 11 do not “appear to be” very different from each other or from the “experimental values” [83-85], but they actually are. The sensitivity of the results to the actual values of the ion-size parameters is significant. This is further verified by what we have seen in literature and reported in this review but also based on communications we have had with many of the researchers – developers of e-EoS (see discussion also in section 5.3). Indeed, taking the diameters from one of the experimental sources and fitting only energy parameters to diverse data yield –no matter the model- densities that are *not* in excellent quantitative agreement with experimental data.

Indeed by far most of the modeling approaches we have studied, density data have been used in parameter estimation and the ion-size parameters are among the fitted parameters.

Thus, it still remains to be seen whether an e-EoS providing excellent densities can be developed without fitting the ion-size parameters and while maintaining equally good results for activity coefficients.

Many activity coefficient approaches including only ion-ion and Born terms (discussed in section 6.3) do not investigate the sensitivity of the results to the ion-size parameters used. In one of the few studies considering this sensitivity, Khomutov [86] used a combination of the extended Debye-Hückel model+Born terms with constant diameter for the ion-ion interactions and a linear concentration dependency of the dielectric constant. Interesting results are presented for 5 chloride electrolytes (halides) which depend strongly on the value used for the "mean ion diameter", with best results obtained using values close to the internuclear distances in molecules of the gaseous halides (rather than using the sum of the hydrate radii). This further illustrates what is seen also for e-EoS that the ion-size parameter values are of importance, and the sensitivity is great not just for the densities but also for the activity coefficients.

Table 11. Diameters in the ion-ion terms (in Å) from various modeling approaches.

Ion	Pauling [83]	Marcus + e-CPA [87,20]	Eriksen eSAFT-VR Mie (Shannon) [71,85]	Shelam eSAFT-VR Mie – with DH [72]	SAFT-VRE (Schreckenberg) [70]	SAFT-VR Morse – with DH [87]	ePC-SAFT Sadowski-1 [60]	ePC-SAFT Sadowski-2 [61]	ePC-SAFT Held [63]	eCPA deHemptinne [18]	QLattice Castier [76]
Li+	1.2	2.08	1.8	1.8942	1.5		2.795	1.8177	2.8449	3.487	1.8526
Na+	1.9	2.36	2.23	2.1607	2.2021	2.2731	2.911	2.4122	2.8232	3.172	2.3222
K+	2.66	2.78	3.04	2.6273	2.6385	1.8334	3.674	2.9698	3.3417	3.315	3.4514
Ca2+	1.98	2.42	2.28	2.7195		3.7627		2.8889	3.1327	2.614	2.8218
Mg2+	1.3	2.09	1.72	2.3783				2.3229	3.2648	1.770	1.2572
Cl-	3.62	3.19	3.34	3.0999	3.0794	2.7339	2.986	3.0575	2.7560	4.096	2.3479
F-	2.72	2.63	2.38	1.8355	1.9344			1.6132	1.7712		2.3005
Br-	3.9	3.37	3.64	3.4887	3.1666	3.0925	3.304	3.4573	3.0707	4.373	2.9526
I-	4.32/4.4	3.65	4.12	3.8870	3.500		3.822	3.9319	3.6672		3.6390

For comparison we can report the values in some other e-CPA models:

Wu and Prausnitz [16] report: Na+: 1.9, Cl-: 3.82

Lin et al. [19]: Na+: 2.59, Cl-: 4.83, Ca2+: 3.26 (in the "full" version of the model). Lin et al. [19] values for e-CPA without SLE data are very different and appear to be not in agreement with other sets:

Na+: 16.05, Cl-: 0.88, Ca2+: 6.14.

6.3 Relative importance of e-EoS terms

One of the most important questions in multi-term (and multi-parameter) models like e-EoS is what is the "correct" relative balance of the various terms for electrolyte systems and how this "relative balance - magnitude" of the terms changes with concentration, temperature and pressure. By "relative magnitude" we mean which terms should be larger or smaller and how these magnitudes should change with the aforementioned conditions. We do not mean the exact values, of course, as these would clearly depend on each model and its parameters. So, it is the qualitative relative magnitude we would be interested to know. As this would certainly help in model development, validation and ultimately selection of the most suitable approach.

Much has been said and written on this topic and it is fair to say that there is no consensus, not even about the relative magnitude of the contributions in the electrolyte part of the models. The latter i.e. electrolyte contributions is also what has been mostly studied.

Several studies have been presented in literature about the combined effect and analysis of relative contributions of ion-ion (DH, MSA) and Born terms. Some of these studies concern e-EoS which also have physical terms such as e-CPA [21-23,18] and e-PC-SAFT or eSAFT-VR Mie [57,59,23,66,67] and others are for activity coefficient models which only include ion-ion and Born contributions. We have mentioned the earlier work of Khomutov [86], but over the recent years systematic studies of the relative contributions of ion-ion/Born effects have been presented by Shilov and Lyaschchenko [SL, 88-90] and Valisko and Boda [VB, 91-94]. In the latter studies, which are with activity coefficient models, typically default ion-size parameters from some experimental source are used. The main differences between the SL and VB approaches are in the choice for the model for ion-ion interactions (Debye-Hückel in SL and a Monte-Carlo approach in VB) and the way the size parameters are estimated. Both use the Born term and a concentration-dependent relative permittivity in all terms. Both groups focus predictions and the size parameters are taken from literature e.g Pauling and Marcus values and no refitting is carried out.

A key conclusion is that a salt composition dependent relative permittivity will affect both the DH/MSA/ion-ion and self (Born) terms when activity coefficients are calculated. In this case, the magnitude of the two terms appear to be comparable (similar order of magnitude) and in opposite directions (positive for Born and negative for ion-ion terms for the ion/mean ionic activity coefficients). If the relative permittivity is constant, the effect of the Born term will disappear entirely for activity coefficients. The actual results will depend a lot on the choice of the expressions for the dielectric constant and especially the values and methods for estimating the ion-size parameters. The effect of the exact theory used for ion-ion effects (DH, MSA or something else) appears to be less crucial compared to all other factors mentioned. These observations are common for both the e-EoS and activity coefficient models, if Born terms and composition dependent R.P are included [18,20-23,57,59,66,67].

This is an important conclusion, but it is worth noticing that approaches (activity coefficients) such as those in refs [22,88-94], despite being entirely predictive with literature values for their ion-size parameters, have no energy parameters at all. In these "simplified" activity coefficient models from SL and VB all ion-ion interactions are obtained directly from the Debye-Hückel or some other ion-ion theory without use of any energy interactions between ions. Energy parameters is a "must" parameter in all electrolyte equations of state but also in "complete" electrolyte activity coefficient models like extended UNIQUAC or e-NRTL (in the latter such parameters are in the physical terms).

The significant effect of the composition dependency of the relative permittivity, especially when considering both ion-ion and self-energy (Born-type) terms, have led some research groups to consider this to be the "only correct solution" and even the explanation for the non-monotonic behavior of the mean ionic activity coefficients for electrolyte solutions. Even in the context of e-EoS, it has been by some stated that failing to include the composition dependency of the dielectric constant (in the Born term), may put "too much pressure" on the fitting parameters and procedure of e-EoS which are based e.g. only on the DH or MSA terms. While these arguments appear, at a first glance, convincing, we cannot be sure that they are entirely correct, at least we cannot be convinced they represent the only way to develop engineering electrolyte models. Many e-EoS have been proposed where the Born term and/or composition dependency of the relative permittivity have been ignored and still successful results are obtained [61-63,70-74], as the physical terms carry the effect otherwise assumed by the Born term (when the relative permittivity depends on salt concentration). For example, in our recent study [23] with eSAFT-VR Mie, we show that when all electrolyte terms are added (Born+ion-ion), their sum is comparable in magnitude to the "physical" term (as the Born term is positive and the ion-ion term is negative for the ion activity coefficients/chemical potentials). Thus, it does look that all forces have a rather delicate balance in electrolyte solutions and with e-EoS models.

Moreover, from the same study [23], it does seem that the sum of the ion-ion+Born contribution only with "real" relative permittivity (maybe together with the "physical" term as well) have the trend of the experimental activity coefficients (the expected curvature). The ion-ion+Born with "constant" relative permittivity appear to be very flat and asymptotic even at high concentration and also twice as large compared to physical part even at high concentrations (surprising, as with increasing concentration electrostatic effects should somewhat diminish and physical effects should become more predominant). These results appear to confirm the need for “real” relative permittivity.

At this stage, we should say that it very often that the salt concentration dependent relative permittivity expressions used in e-EoS and activity coefficient models are rather empirical ones. It is not clear whether the compositional derivatives from such empirical expressions that are needed in e-EoS will be accurate. Moreover, it is typically assumed that in thermodynamic models we can use the total reduction of the relative permittivity with respect to salt concentration. This is, of course, convenient but not necessarily correct as it has been mentioned [53] that the dielectric concentration dependency consists of a thermodynamic and a kinetic depolarization term. It is unclear whether the latter should be included in thermodynamic models. Moreover, empirical correlations of the concentration dependency of the dielectric constant may not always yield qualitatively correct volume derivatives, as shown in literature [53]. Still when a large number of salts are considered, these empirical correlations for the relative permittivity are often used.

The concentration dependency of the relative permittivity continues to be a debated topic, with or without the use of the Born term. Fawcett and Tikanen presented an MSA+HS model [95,96] and they comment that a very significant improvement in the MSA description of electrolyte solutions is obtained if we include the concentration dependency of the solvent permittivity in the model. Their model does not have Born term but they show that the hard-sphere term counterbalances the ion-ion interactions from MSA.

Finally, it is worth mentioning the model presented by Fraenkel in 2010 [97] called DH-SiS, recently extended also to electrical conductivity [98]. DH-SiS is considered to be a modified Debye-Hückel theory, aiming to extend the original DH theory to size-dissimilar ions, thus permitting calculations for many electrolyte families up to moderately high concentrations. It is an activity coefficient model without other terms than the electrostatic contributions. Unlike the models by SL and VB, there is no Born term in the Fraenkel model and Fraenkel argues why the dielectric constant of the solvent should be used without accounting for concentration effects. The Fraenkel model contains several size parameters, which are fitted to experimental data. Especially in the fitting range, the Fraenkel model provides good results for mean ionic activity coefficients for many aqueous salt solutions, as shown in many publications. Fraenkel has insisted that his model is physically more correct than previous versions of DH or primitive approaches and with physically correct values for the ion size parameters. VB and Fraenkel have discussed the necessity for the Born term and the concentration dependent dielectric constant [99,100] as well as debated the importance of the Debye-Hückel equation and the balance between ion-ion and ion-water effects. VB use both ion-ion and ion-water terms, but for the former they employ a Monte-Carlo (MC) approach which they insist is much better than DH, something Fraenkel clearly disagrees. Fraenkel can get the minimum in the activity coefficients of salts with an ion-specific DH (using fitted ion-specific size parameters) without use of ion-water solvation/Born terms and without concentration dependent dielectric constant. VB's approach –compared to Fraenkel- differs in almost all aspects: another ion-ion theory, Born is used, predictive and average ion-parameters and finally concentration dependent dielectric constant. Fraenkel obtained acceptable results also for some salts with theoretical and not fitted values of the ion-size parameters. Fraenkel believes that several aspects of the various models may have self-cancellation effects. Zarubin [101] and others have showed that the results of DH-SiS become progressively worse at higher concentrations (and beyond the fit of ion-specific parameters). This is something which Fraenkel does not attribute to ion-solvation or to ion-pairing, but maybe to non-electrostatic effects which can be important at higher concentration (and even contribute to the minimum in activity coefficients for certain aqueous salt solutions).

We conclude that there is no consensus on the use of composition dependent R.P and of the Born term, neither in the world of electrolyte equations of state nor in activity coefficient models proposed for electrolytes. Much more work is needed. The Born equation will be discussed in a forthcoming review.

7. Conclusions

A critical and comparative evaluation of electrolyte equations of state (e-EoS) has been presented, with emphasis on e-versions of cubic and CPA approaches. Some e-SAFT and other methods have also been briefly discussed. The modeling and validation approaches of the various models differ greatly, especially in the electrolyte part. It is clear from this review that development of e-EoS is possibly one order of magnitude more complex (if not more) compared to models for non-electrolyte solutions. It does not appear that there is consensus on which modeling approach should be chosen, which database should be used for development and validation or which is the appropriate balance of contributions of the e-EoS terms for electrolyte solutions. There are also different views on the capabilities and limitations of the approaches depending on the source.

Nevertheless, our reading of the literature and our own studies (past and the ones presented in this review) allow us to make some concluding remarks on the equations of state for electrolytes. Even these remarks we expect could be contested but they nevertheless represent our views based on own and others' experiences.

Here are our major conclusions summarized in the following 10 points:

1. It appears that, for electrolyte solutions, due to the dominance of electrostatic forces, the choice of the physical term in e-EoS appears to be relatively insignificant, especially compared to other aspects of development for electrolyte systems. If the solvent properties especially water are well-represented (both vapor pressure and densities), then cubic, CPA, SAFT or other physical terms appear to perform equally well. A SAFT approach has a small advantage that the "ion diameter" appears in both physical and electrostatic terms. For e-Cubic and e-CPA approaches, different possibilities exist for the link between

ion diameter and ion co-volume and an appropriate choice should be carefully made, as the results can be highly sensitive on the values of the ion-size/co-volume parameters.

2. It appears that the full Debye-Hückel and MSA equations perform, all other parameters being equal, similarly for electrolyte solutions and it is difficult to choose one over the other. We observe with interest that since its first use in e-PC-SAFT in 2005 and about 100 years since its development, the full Debye-Hückel has gained much attention in the 21st century and is used in many electrolyte EoS, also beyond those summarized in this review. Both the DH and MSA models include an ion-size parameter, which can be taken from literature or fitted to data. More important than which ion-ion term is used, is whether a concentration dependency is used or not for the relative permittivity, see next.
3. The role of the relative permittivity in these e-EoS has been heavily debated. Whether a constant value for the solvent should be used or whether we should have a concentration-dependent value (which is in agreement with relative permittivity data) is not clear. Either approach has merits and both have been used in various literature electrolyte models. Which one is to be preferred after parameter estimation and when physical terms have been included in complete electrolyte models like e-EoS has not been established. A related issue which is not clear is whether we are permitted to include a composition dependency of the relative permittivity after the derivation of the electrostatic contribution to Helmholtz energy e.g. in the Debye-Hückel context, if this derivation is based on a constant relative permittivity assumption (as typically done). Ignoring the assumption used in the derivation is not thermodynamically inconsistent but is it physically correct ?
4. The Born-type (self-energy) term has been debated as well and it is very much connected to the relative permittivity concentration dependency mentioned in point 3. If the latter is ignored, i.e. if we use a constant value for the relative permittivity of water, the Born term does not contribute to phase equilibria, only to the calculation of the solvation energies.
5. Mean ionic and osmotic activity coefficients as well as densities are the “first properties” to model. Good densities require that both ion-size and energy parameters are fitted also to density data. It appears that the sensitivity of ion-size parameters especially with respect to densities is significant. Even though most models, when fitted, yield ion-size parameters close to some experimental set (Pauling, Marcus, Shannon) direct use of these values instead of the fitted ones result to not so satisfactory densities. Future studies are needed to clarify this point.
6. Very few models have considered salt solubilities, hydrated salts and solid-liquid equilibrium. The challenge of having reliable standard state properties is significant and, in most cases, good SLE require that the standard state properties are included in parameter estimation together with the other parameters and that SLE data are also included in the parameter estimation database.
7. Both for SLE but also for activity coefficients, we see serious challenges at higher temperatures and higher concentrations. This is systematic with all modeling approaches indicating that ion-

pairing may play a significant role at these conditions. Few studies have been proposed for including ion-pairing, and most of them do this indirectly via ion-water association or ion-ion dispersion interactions. Only recently a research group has included the Bjerrum theory and an extra term in an e-EoS and the first results appear promising. In general, the extent of importance of ion-association, whether sites should be assigned to ions and whether ion-solvation needs a treatment different than Born are issues which have not been clarified. It is also important to mention that thermal properties may help in the parameterization of the EoS models at elevated temperatures, as it has been the case for electrolyte activity coefficient models like extended UNIQUAC. It appears that such thermal properties are neglected in the development and/or the validation of e-EoS models; the reasons for this not being entirely clear to us.

In this context, we can mention that in many cases the quality of experimental data may affect the models' parameterization and validation. This is especially important when a model is fitted to get specific parameters. We have noticed significant uncertainties in reported data, especially for LLE and SLE. Thus, special care is needed when selecting experimental data for comparison and model fitting.

8. A major challenge of all modeling approaches, which brings all e-EoS to their "borders", are mixed solvents and particularly mixed solvent-salt LLE. It has been very difficult to describe such systems and types of phase equilibria correctly. The Born term, concentration-dependent R.P and ion-pairing may all play an important role here, but exactly which role and how they should be used in e-EoS is not clear.
9. All approaches based on the Debye-Hückel theory follow a solution of the linearized Poisson-Boltzmann (LPB) equation. Even the full DH theory, despite being seen as complete and elegant, is based on LPB. In principle, LPB should be used "at lower concentrations" where its assumptions that lead to linearization are valid. Which are these "lower concentrations" is not clear. Few systematic studies compare the full PB and LPB and we are further working on this topic and report soon our conclusions. Differences between full PB and LPB may be expected at symmetric/low valency vs. asymmetric/high valency salts, again a topic not much studied. Both the DH and MSA theories are based on the so-called "primitive approach" – solvent not as "molecule" but described via its R.P. How such theories compare to the "non-primitive theories" and whether the latter have advantages are still big questions, especially very few engineering non-primitive theories have been developed [102,103] and they have not been applied extensively to a wide range of systems. A specific aspect that has been criticized, also when compared to corresponding terms from non-primitive theories, is the Born term – how accurately does it represent self-energy or ion-solvation effects ? This is not clear. We will be discussing the Born term in a separate review.
10. Despite covering a number of topics, in order to keep it at a certain length, this review has not discussed (much) a number of important areas of electrolyte thermodynamics, all of them of potential importance to the development and validation of e-EoS. These are the field of weak

electrolytes e.g. aqueous mixtures of acid gases with many polar chemicals, the prediction of thermal and other derivative properties, transport properties and in particular electrical conductivity and finally the role that molecular simulation and individual ion activity coefficients may play in understanding the forces-terms and the development of e-EoS. Partial discussions of these topics can be found in [2,7,98].

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List of Abbreviations

AMV	apparent molar volumes
CPA	Cubic-Plus-Association equation of state
DH	Debye-Hückel theory for ion-ion interactions
e-EoS	electrolyte equation of state
EoS	equation of state
HS	hard-sphere term
LLE	liquid-liquid equilibria
LR	Lewis-Randall framework
MIAC	mean ionic activity coefficients

MM	McMillan-Mayer framework
MSA	mean-spherical approximation (theory for ion-ion interactions)
MWS	Myers-Wood-Sandler e-EoS model
NRTL	Non-random two-liquid (activity coefficient) model
PDH	Pitzer-Debye-Hückel theory
R.P	static relative permittivity or dielectric constant
SAFT	statistical associating fluid theory
SLE	solid-liquid equilibrium
SR	short-range (term often used as additional term in e-EoS)
VLE	vapor-liquid equilibrium

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