Analysis and Applications of the Electrolyte Cubic Plus Association Equation of State

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Analysis and Applications of the Electrolyte Cubic-Plus-Association Equation of State

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September 2019

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Preface

This thesis is submitted as a partial fulfillment of the requirements for the Ph.D. degree at Technical University of Denmark. The work was carried out from October 2016 to September 2019 at the Center for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering, under the supervision of Professor Georgios M. Kontogeorgis, Associate Professor Xiaodong Liang and Associate Professor Nicolas von Solms. This work is supported by the Department of Chemical and Biochemical Engineering, Technical University of Denmark and China Scholarship Council.

The objectives of the presented work are to apply and analyze the electrolyte Cubic Plus Association Equation of State, especially modeling several electrolyte solutions of quaternary ammonium salts, gas solubility in aqueous electrolyte solutions, and activity coefficients of individual ions in aqueous solutions.

Several different people should be thanked for their positive contribution to my past three years. First of all, I would like to thank my supervisor Professor Georgios M. Kontogeorgis for the opportunity to work on this project, and the enormous help and support he has provided me during the study. Next, an enormous thanks to Associate Professor Xiaodong Liang for enormous help and support during the study, whenever I came with a thermodynamic question. An enormous thanks to Associate Professor Nicolas von Solms and Associate Professor Kaj Thomsen for many constructive suggestions.

I am grateful for the ongoing support and guidance that supervisors have given, for supervisors' enthusiasm and ideas, and for always encouraging me to move forward. Thanks are also given to all the colleagues in CERE for providing a friendly and happy working environment. In particular, I would like to thank Louise, Patricia and Christian for all the support and hard work they do in order for me
to just focus on my project, it is invaluable.
Finally, I wish to thank my family for their support, and especially I would like to thank my wife Xiaohong Xu for taking care of our kid Xulang Sun while I have been busy.

Copenhagen, September 2019
Li Sun
Abstract

Due to the complexity and wide industrial application of the electrolyte solutions, both experimental and theoretical studies have attracted great interest. The lack of reliable thermodynamic data of aqueous electrolyte solutions with a wide range of temperature and pressure can be sometimes resolved by using thermodynamic models. The electrolyte Cubic Plus Association (CPA) Equation of State (EOS), e-CPA, is an extension of the CPA EOS to electrolytes through the addition of the Debye-Hückel theory for the ion-ion electrostatic interactions, and the Born term for ion solvation.

The main aim of this thesis is to analyze the e-CPA EOS and apply e-CPA to a range of electrolyte systems.

In the first part of this thesis, thermodynamic modeling of the aqueous solutions of quaternary ammonium salts (QAS) and metal halide salts are presented.

For QAS systems (single-salt systems), the ion size and adjustable model parameters are obtained by fitting the experimental data of mean ionic activity coefficients and osmotic coefficients. Several other thermodynamic properties of aqueous solutions, such as relative static permittivity, liquid density and saturation pressure, are subsequently predicted by e-CPA. The results show that the model can satisfactorily correlate the mean ionic activity coefficients and osmotic coefficients. The reliability of experimental data, parameter estimation approaches and the ion size effects are extensively discussed.

For metal halide salt systems (multi-salt systems), the adjustable model parameters of single-salt systems are subsequently used for modeling of multi-salt systems directly. The results show that e-CPA can predict well the mean ionic activity coefficients of aqueous multi-salt solutions using single-salt interaction parameters.

The second part of this thesis presents thermodynamic modeling
studies on the gas solubilities in aqueous electrolyte solutions. The adjustable parameters are obtained by fitting the experimental data of gas solubilities in single-salt solutions. The results show that the model can reasonably correlate gas solubilities over a wide range of conditions for most systems. The model is then used to predict the gas solubility in multi-salt (metal halide salt) solutions, and a reasonable performance is also achieved. The salting-in/salting-out effects and the various factors affecting the results are finally studied.

At the last part of this thesis, a modeling study is carried out for individual ion activities in aqueous electrolyte solutions with e-CPA and other approaches including the ‘extended version of Debye–Hückel + Born’ model, and the ‘MSA+Born’ model.
Prorumé


Hovedformålet med denne afhandling er at analysere e-CPA EOS og anvende e-CPA på nogle elektrolytsystemer.


Den anden del af denne afhandling præsenterer en termodynamisk modelleringsundersøgelse af gasopløseligheden i vandige elektrolytopløsninger.

De justerbare parametre opnås på basis af de eksperimentelle data for gasopløseligheder i opløsninger med et enkelt salt. Resultaterne viser, at modellen på en tilfredsstillende måde kan beskrive gasopløseligheder over en lang række betingelser og for de fleste systemer. Modellen bruges derefter til at forudsige gasopløseligheden i multisaltopløsninger (metalhalogenidsalt), og der opnås tilfredsstillende resultater. Salting-in / salting-out-effekterne og de påvirkende faktorer undersøges også.

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## List of Abbreviations and Symbols

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<th>Names</th>
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<tr>
<td>AMSA</td>
<td>Mean Spherical Approximation for Aqueous Electrolytes includes Ionic Hydration and Association</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>calcium chloride</td>
</tr>
<tr>
<td>CH₄</td>
<td>methane</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>ethane</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>propane</td>
</tr>
<tr>
<td>CPA</td>
<td>Cubic-Plus-Association</td>
</tr>
<tr>
<td>CO₂</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>DH</td>
<td>Debye-Hückel</td>
</tr>
<tr>
<td>EOS</td>
<td>Equation of State</td>
</tr>
<tr>
<td>e-CPA</td>
<td>electrolyte Cubic-Plus-Association</td>
</tr>
<tr>
<td>e-NRTL</td>
<td>electrolyte Non-Random Two Liquid model</td>
</tr>
<tr>
<td>H₂S</td>
<td>hydrogen sulfide</td>
</tr>
<tr>
<td>KCl</td>
<td>potassium chloride</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>magnesium chloride</td>
</tr>
<tr>
<td>MSA</td>
<td>Mean-Spherical-Approximation</td>
</tr>
<tr>
<td>MPT</td>
<td>Modified Patel-Teja</td>
</tr>
<tr>
<td>N</td>
<td>number of data points</td>
</tr>
<tr>
<td>N₂</td>
<td>nitrogen</td>
</tr>
<tr>
<td>NaCl</td>
<td>sodium chloride</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>Sodium Sulfate</td>
</tr>
<tr>
<td>NRTL</td>
<td>Non-Random Two Liquid model</td>
</tr>
<tr>
<td>Np</td>
<td>number of data points</td>
</tr>
<tr>
<td>P</td>
<td>pressure [Pa]</td>
</tr>
<tr>
<td>PC-SAFT</td>
<td>Perturbed-Chain statistical associating fluid theory</td>
</tr>
<tr>
<td>PMSA</td>
<td>primitive MSA term</td>
</tr>
<tr>
<td>PR</td>
<td>Peng-Robinson</td>
</tr>
<tr>
<td>PT</td>
<td>Patel and Teja</td>
</tr>
</tbody>
</table>
QAS  quaternary ammonium salts
R    ideal gas constant (8.3144621 [J/mol/K])
RAD  relative average deviation
RK   Redlich-Kwong
RPM  restricted primitive model
R₄N⁺ quaternary ammonium cations
SAFT Statistical associating fluid theory
SAFT-VRE Statistical Associating Fluid Theory with Variable Range for Electrolytes
SAFT-LJ Lennard-Jones SAFT
SCH  Semi-Clathrate Hydrate
SRK  Soave-Redlich-Kwong
T    temperature [K]
TB   Trebble–Bishnoi
TBA⁺  Tetra-n-butyl Ammonium Cation
TBAB  Tetra-n-butyl Ammonium Bromide
TBAC  Tetra-n-butyl Ammonium Chloride
TBAF  Tetra-n-butyl Ammonium Fluoride
TBAX  Tetra-n-butyl Ammonium Halides
TBP⁺  Tetra-n-butyl Phosphonium Cation
TBPB  Tetra-n-butyl Phosphonium Bromide
TEA⁺  Tetra-n-ethyl ammonium Cation
TMA⁺  Tetra-n-methyl ammonium Cation
TMAB  Tetra-n-methyl ammonium bromide
TEAB  Tetra-n-ethyl ammonium bromide
TPA⁺  Tetra-n-propyl ammonium Cation
TPAB  Tetra-n-propyl ammonium bromide
UNIQUAC universal quasichemical model
V    volume [m³]

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Names</th>
</tr>
</thead>
<tbody>
<tr>
<td>A⁺</td>
<td>residual Helmholtz energy</td>
</tr>
<tr>
<td>A⁺SRK</td>
<td>residual Helmholtz energy</td>
</tr>
</tbody>
</table>
contribution for the cubic Soave–Redlich–Kwong EOS [J/mol]

$A_{\text{ASSOC}}$ residual Helmholtz energy contribution for association [J/mol]

$A_{\text{DH}}$ residual Helmholtz energy contribution from the Debye-Hückel theory [J/mol]

$A_{\text{Born}}$ residual Helmholtz energy contribution Born hydration model [J/mol]

$C_i$ Peneloux volume correction parameter of component $i$ [m$^3$/mol]

$N_A$ Avogadro constant ($6.0221415 \times 10^{23}$ [1/mol])

$p_w^{\text{sat}}$ saturation pressure of water

$P_{ij}$ probability of molecule $i$ and $j$ to be hydrogen bonded

$P_i$ probability of the molecule $i$ to be bonded to any of the molecules

$T_{\alpha}$ an adjustable parameter of the temperature dependency [K]

$T_C$ critical temperature [K]

$T_r$ reduced temperature

$T_{\text{ref}}$ reference temperature (298.15 K) an adjustable parameter of the temperature dependency [K]

$T_{\Delta U_{ij}}$ an adjustable parameter of the temperature dependency [K]

$X_{A_i}$ fraction of site A on molecule $i$ that is not bonded to any other site

$Z_{ij}$ coordination number of molecule $i$

$Z_i$ charge of ion $i$

$a$ SRK temperature dependent energy parameter $[\text{Pa} \cdot \text{m}^6/\text{mol}^2]$

$b$ CPA co-volume [cm$^3$/mol]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>e</td>
<td>the elementary charge.</td>
</tr>
<tr>
<td>n</td>
<td>total amount of component [mol]</td>
</tr>
<tr>
<td>v</td>
<td>molar volume [m³/mol]</td>
</tr>
<tr>
<td>κ</td>
<td>inverse Debye length [1/m]</td>
</tr>
<tr>
<td>κ₀</td>
<td>usual inverse Debye length [1/m]</td>
</tr>
<tr>
<td>ρ</td>
<td>molar density of fluid [mol/m³]</td>
</tr>
<tr>
<td>a_w</td>
<td>activity of water</td>
</tr>
<tr>
<td>c₁</td>
<td>pure component temperature dependence parameter for Soave’s α(T)-function</td>
</tr>
<tr>
<td>dᵢ</td>
<td>hard-sphere diameter of ion i [Å]</td>
</tr>
<tr>
<td>gᵢ</td>
<td>Kirkwood g-factor for molecule i</td>
</tr>
<tr>
<td>g(ρ)</td>
<td>radial distribution function</td>
</tr>
<tr>
<td>rᵢ</td>
<td>radius of the ion i [Å]</td>
</tr>
<tr>
<td>αᵢ</td>
<td>linear dependency in interaction energy calculation [K]</td>
</tr>
<tr>
<td>αⱼᵢ</td>
<td>NRTL non-randomness parameter</td>
</tr>
<tr>
<td>α₀,i</td>
<td>molecular polarizability of molecule or ion i [10⁻⁴⁰ C · m² · V⁻¹]</td>
</tr>
<tr>
<td>cL</td>
<td>molar concentration of salt [mol/L]</td>
</tr>
<tr>
<td>vₑOₛ</td>
<td>molar volume calculated from e-CPA [m³/mol]</td>
</tr>
<tr>
<td>gₑ,∞</td>
<td>excess Gibbs energy at infinite pressure [KJ/mol]</td>
</tr>
<tr>
<td>k_B</td>
<td>Boltzmann constant (1.3806503 × 10⁻²³ [J/K])</td>
</tr>
<tr>
<td>rᵦ_Born,i</td>
<td>Born radius of the ion i [Å]</td>
</tr>
<tr>
<td>xᵢ</td>
<td>mole fraction of component i</td>
</tr>
<tr>
<td>φ</td>
<td>Internal C-O-H angle</td>
</tr>
<tr>
<td>θᵢⱼ</td>
<td>hydrogen bond angle bond between molecule j in shell around molecule i and the second shell neighbor</td>
</tr>
</tbody>
</table>
angle between the dipole moments of molecule i and j in the hydrogen bond network

$\gamma_{ij}$

dipole moment of water in vacuum [C.m]

$\mu_0$

dipole moment of component i in vacuum [C.m]

$\mu_{i,0}$

binary interaction parameter between solvent and gas

$k_{ij}$

CPA reduced energy parameter $(a_0/Rb)$ [K]

$\Gamma$

Change in interaction energy between like and unlike interactions [J/mol]

$\Delta U_{ij}$

binary interaction parameter at the reference temperature [J/mol]

$\Delta U_{ij}^{ref}$

association strength (equilibrium constant) between site A on molecule i and site B on molecule j [m$^3$/mol]

$\Delta_{AB}ij$

association volume between site A on molecule i and site B on molecule j

$\beta^{AB}ij$

association energy between site A on molecule i and site B on molecule j [bar.L/mol]

$\varepsilon^{AB}ij$

packing factor; $\eta = b/4v$

$\eta$

static permittivity relative to vacuum

$\varepsilon_r$

vacuum permittivity (8.85419 × 10$^{-12}$ [F/m])

$\varepsilon_0$

infinite frequency permittivity relative to vacuum

$\varepsilon^\infty$

mean ionic activity coefficient

$\gamma^m_{\pm}$

mean ionic activity coefficient (rational)

$\gamma_{\pm}$
\( \Phi \) osmotic coefficient

\( \omega_{\Delta U_{ij}} \) linear dependency in interaction energy calculation \([\text{K}]\)
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5.14 e-CPA performance of activity coefficients for electrolyte solution of CaCl$_2$
5.15 e-CPA performance of activity coefficients for electrolyte solution of MgCl$_2$
5.16 e-CPA performance of activity coefficients for electrolyte solution of MgCl$_2$
solution of Na$_2$SO$_4$

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Chapter 1. Introduction

When electrolytes (salt or some ionic compounds) are dissolved in water or other solvents (such as ethanol and other organic solvents), they dissociate into ions that have lost or gained electrons partially. The formed solution called electrolyte solution or ionic solution is electrically conductive. Even at very low electrolyte concentrations, the presence of the charged ions has the consequence that the non-ideality in electrolyte solutions is much more pronounced than in non-electrolyte solutions [1]. The difference is mostly due to the dissociated ions. In electrolyte solutions, there are basically two different species: dissociated ions and molecules. There are, thus, three different interactions in electrolyte solutions: molecule-molecule, ion-ion and molecule-ion. A strong electrolyte can dissociate completely while a weak electrolyte only dissociates partially. In weak electrolyte solutions, the solute (such as some weak acids) not only exists as cations and anions, but also as molecules. The number of ions and solute molecules in the solution is determined by the dissociation equilibrium constant of the solute.

Water is the most common solvent for electrolytes. The study of electrolyte systems, particularly of aqueous electrolyte solutions, has a wide diversity of applications in chemical, environmental, and biological industries. In nature, electrolytes are important in geological systems. Thermodynamic study of aqueous electrolyte solutions is important for gas hydrate studies. Gas hydrate is a solid ice-like form of water that contains gas molecules in its molecular cavities [2]. Under the appropriate pressure and temperature conditions, gas hydrates may be a significant hazard in natural gas pipelines, which can result in pipeline block and affect safe operation of pipeline. On the other hand, gas hydrates also have considerable potential as storage and separation media for various gases. Promotion and inhibition are, therefore, equally important in hydrate studies. Salt
Introduction

is a relatively common additive for hydrate formation. Some metal halide salts (e.g. sodium chloride: NaCl) are well-known thermodynamic hydrate inhibitors [3], because they can move the conditions required for gas hydrate formation to lower temperatures and (or) higher pressures by reducing the water activity.

In 1940, Fowler and coworkers [4] discovered that the addition of some quaternary ammonium salts (e.g. Tetra-n-butyl ammonium halides: TBAX) in water, could result in the formation of crystals at room temperature. This formed hydrate was named semi-clathrate hydrates (SCH). In the structure of SCH, the anions of salts coupled with water molecules build a clathrate framework (formed by hydrophilic beads). The cation is embedded in the framework cavities (formed by hydrophobic beads), while the small guest gas molecules could be contained in empty pentagonal dodecahedron cages. This special structure makes SCH more stable than usual hydrates [5]. SCH have attracted attention in recent years, because of the application possibilities such as gas separation, thermal storage, CO₂ sequestration and CH₄ transportation [6].

In order to be entrapped in the hydrate cage, the guest molecules must have a suitable size. The guest molecules need to be larger than argon, and smaller than n-butane. Normally, the following gases can be captured in hydrates clathrate: methane (CH₄), ethane (C₂H₆), propane (C₃H₈), nitrogen (N₂), carbon dioxide (CO₂), hydrogen sulfide (H₂S) [7].

Besides gas hydrate systems, the study of gas in aqueous electrolyte solution is also important for certain industrial applications.

One important way of reducing CO₂ emissions is to capture CO₂ from emission sources and inject it into deep saline formations. The injected CO₂ dissolves into the saline pore waters and forms an aqueous solution. Some inorganic salts (sodium chloride: NaCl, potassium chloride: KCl, calcium chloride: CaCl₂, magnesium chloride: MgCl₂, sodium sulfate: Na₂SO₄), water (H₂O), and CO₂ are the most common species in geological fluids [8]. CH₄, another
important greenhouse gas, has also been reported in many geological fluids [9]. As a kind of accompanied gas, N₂ is one of the major components of flue gas emitted from power plants [10]. C₂H₆ is an important part of natural gas and guest gas in natural gas hydrates [11].

Lack of reliable thermodynamic data of aqueous electrolyte solutions in a wide range of temperature and pressure can be accounted by using thermodynamic models. Thermodynamic modeling, especially for the phase equilibria of aqueous electrolyte systems is needed in order to design, simulate, and optimize processes with electrolyte systems [12]. The ions interact with electrostatic forces which are of much longer range than those involved in the interactions of neutral molecules, and this effect is stronger the greater the charge density of the ions.

Based on the classical theory Debye-Hückel (DH) model [13], some researchers proposed semi-empirical models for electrolyte solutions, and especially the proposed activity coefficient models have a wide application range. The most well-known activity coefficient models are the Pitzer model [14], the electrolyte Non-Random Two-Liquid (e-NRTL) model [15], and extended universal quasichemical (UNIQUAC) model [16].

Based on the Helmholtz free energy, some Equations of State (EOS) have been combined with electrostatic terms and are used for the calculation of thermodynamic properties in electrolyte systems. Some proposed electrolyte EOS include those from the Harvey and Prausnitz's [17], by Aasberg-Petersen et al.'s [18], Zuo and Guo's model [19], Søreide and Whitson's model [20], as well as electrolyte EOS based on statistical associating fluid theory (SAFT) [21-23].

Maribo-Mogensen et al. [24] extended the Cubic-Plus-Association (CPA) EOS, which was proposed by Kontogeorgis et al. [25], to mixtures containing electrolytes. In e-CPA, the residual Helmholtz energy includes contributions from CPA, the DH theory [13] (for the long-range interaction of the ions) and the Born equation [26] (for
ion solvation).
The aim of the work presented in this thesis is to analyze this electrolyte EOS and apply it to electrolyte systems not considered before.

In the modeling of electrolyte systems, the results are thoroughly analyzed with emphasis on the capabilities and limitations of the model, the reliability of the experimental data, and the parameter estimation approaches employed. Finally, activity coefficients of individual ions are also investigated using various electrolyte theories and e-CPA and the relative contributions of the various electrostatic and physical terms are evaluated.

This project is a part of development of the electrolyte e-CPA. More specifically, this PhD project focuses on the investigation of the model performance of aqueous solutions of quaternary ammonium salts, aqueous multi-salt solutions, gas solubility in aqueous solution of metal halide salts and quaternary ammonium salts (QAS), and also the activity coefficients of individual ions in aqueous solutions.

Several of the results have been published in two peer-reviewed journal papers. The manuscripts are referenced in this thesis as References [27, 28].

An overview of attended conferences and publications, along with other PhD activities, are presented in Appendix A. One more manuscript is under review.

The thesis is divided into three parts; an introduction and literature review (Chapter 1-2), a part related to thermodynamic modeling for aqueous electrolyte solutions (chapter 3), a chapter related to modeling of gas solubility (chapter 4), and finally the investigation of activity coefficients of individual ions and analysis of terms of the models (Chapter 5), as well as a conclusion Chapter 6.

A more detailed overview of the chapters and their content is given below. This current introduction Chapter 1 briefly introduces the background and characteristics of electrolyte systems, applications and thermodynamic models for electrolyte solutions. Furthermore, the motivation and structure of the thesis are presented.
Chapter 2 introduces the major theories of electrostatic interactions; the DH theory, extended version of DH model, MSA, Born equation and e-CPA.

In Chapter 3, the water+salt/salts systems are modeled using e-CPA. The modeling of aqueous multi-salt solutions for inorganic salts, and the modeling of aqueous single-salt solutions for QAS are included. The discussion of modeling performance and parameter affection is also presented.

In Chapter 4, solubility of some gases in aqueous electrolyte solutions are correlated and predicted using e-CPA. The salting effect of different salts are analyzed and discussed.

Chapter 5 is the investigation of single-ion activities using the classical theories and e-CPA, as well as a discussion of various theories and analysis of the terms involved.
Chapter 2. Thermodynamic Models

This chapter presents the thermodynamic models which are used in this work.

Chapter structure and contents:
2.1 Debye-Hückel Theory
2.2 Born Equation
2.3 Ion Association Theory
2.4 Extended version of Debye–Hückel
2.5 Mean Spherical Approximation
2.6 Electrolyte Cubic Plus Association
Thermodynamic Models

**Introduction**

Thermodynamic models can mathematically describe the properties and the phase behavior of electrolyte solutions. In order to properly model electrolyte systems, different types of interactions should be taken into account.

Most models for electrolyte solutions are based on classical thermodynamic theories (Debye-Hückel theory [13], mean spherical approximation (MSA) [29] and Born equation [26]). The most used theoretical approaches are the activity coefficient models (e.g. Pitzer model [14], electrolyte Non-Random Two Liquid model (e-NRTL) [15], and extended universal quasichemical (UNIQUAC) model [16]), the theory of statistical mechanics [29] (integral equation theory, perturbation theory and molecular simulation) and the electrolyte EOS.

The first really successful model for the electrostatic interactions between ions in aqueous electrolyte systems was the Debye-Hückel model [13].

The Debye-Hückel model is described as a ‘dielectric continuum model’. The electrostatic interactions between charged ions only represent the long-range interactions and not the short-range interactions. The interactions between ions and water are not described by the Debye-Hückel model. The solvent only plays a role due to its relative static permittivity (dielectric constant) and its density (primitive theory approach). The Debye-Hückel model only represents the electrostatic interactions and should be combined with a term for short and intermediate range interactions.

In order to extend the application scope of Debye-Hückel, some modifications and improvements (e.g. adjustable parameters) are required.

Stokes and Robinson proposed the theory of ionic hydration [30]. They stated that some solvent molecules in solution could combine with solute ions through a certain way of action to form solvated ions, while other solvent molecules not combined with ions were free molecules.
Born [26] proposed an equation for the interaction between an ion and the surrounding solvent, as around an electrical charge there is an electrostatic field. Based on the classical theory, some researchers proposed semi-empirical models. Activity coefficient models have the advantages of a wide application range with often good accuracy. The most well-known activity coefficient models are Pitzer model [14], e-NRTL model [15], and extended UNIQUAC model [16]. Based on statistical thermodynamics, the integral equation theory and the perturbation theory have been proposed for electrolyte systems. By solving the particle in the solution of radial distribution function solution model, MSA [29] is derived and is today a broadly used model. The model treats ions as charged hard spheres, solvent as a continuum, and the thermodynamic properties are obtained by solving the integral equation. Based on Helmholtz free energy, EOS and electrostatic terms are combined together for the calculations of thermodynamic properties and phase equilibrium of electrolyte solutions. Some typical electrolyte equations of state are Harvey and Prausnitz's model [17] (based on a short-range perturbed term with Lennard-Jones potential, the MSA term [31], and Born term [26]), Aasberg-Petersen et al.'s model [18] (based on the four-parameter ALS EOS [32, 33] plus a modified Debye-Hückel term [13]). Zuo and Guo's model [19] (based on Patel-Teja (PT) EOS and Debye-Hückel term), Søreide and Whitson's model [20] (extended the Peng–Robinson (PR) EOS by making modifications for binary interaction parameters of aqueous and non-aqueous phases respectively) and electrolyte EOS based on the statistical associating fluid theory (SAFT) [21-23]

2.1 Debye-Hückel Theory

In 1923, Debye and Hückel [13] proposed a theory, which is a very important achievement in the study of modern electrolyte solution
theory. The Debye-Hückel theory is a typical primitive model (treats the solvent as a continuous dielectric medium), which is based on electrostatic interaction between ions. This theory regards solvent as a continuous medium, and the free energy of the system is the sum of coulombic attraction between positive and negative solute ions without considering short-range repulsive forces. The influence of solvent on the free energy of the system is corrected by introducing the dielectric constant. The Debye-Hückel theory regards ions as point charges and obeys the Poisson's equation [34] of electrostatic principle. The charge distribution obeys the Maxwell-Boltzmann distribution [35], which is mainly applied to the non-associated electrolyte solution where only positive and negative ions exist in the system.

In the Debye-Hückel theory, the electrostatic interaction between positive and negative ions is expressed through Coulomb's law:

\[
F = -\frac{1}{4\pi\epsilon_0\epsilon_r} \frac{e^2}{r^2}
\]

(2.1)

In Eq. (2.1), \( e \) is the electronic charge, \( \epsilon_0 \) is the permittivity in vacuum, \( \epsilon_r \) is the relative permittivity of the solvent.

Debye and Hückel combined the Poisson equation and the Boltzmann equation thereby eliminating the charge density. The resulting Poisson-Boltzmann equation was solved for the electrical potential. Debye and Hückel finally arrived at an excess Helmholtz function for an ideal solution of charged ions. The molar excess Helmholtz function for the electrostatic interactions can be expressed by the equation:

\[
\frac{A_{EX}}{RT} = -\frac{1}{3} \sum \chi_i Z_i^2 s k \kappa \chi (\kappa a_i)
\]

(2.2)

In Eq. (2.2), \( Z_i \) is the charge of ion \( i \), \( k \) is the Boltzmann constant, \( R \) is gas constant, and \( T \) is the temperature in Kelvin, \( a_i \) is the distance of closest approach to the ion \( i \). It is expected that \( a_i \) is larger than the radius of the ion, because the ions are thought to be surrounded by water that gives the ions a larger radius than the bare ion. The term \( s \) is defined by:
Thermodynamic Models

\[ s = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r kT} \]  
(2.3)

where \( \kappa \) is the inverse of screening length (if the distance is beyond this screening length, the Coulomb interactions can be, in principle, ignored).

The expression for \( \kappa \) is:

\[ \kappa = \left( \frac{e^2 N_A^2}{\varepsilon_r \varepsilon_0 RT V} \sum_{i} n_i Z_i^2 \right)^{1/2} \]  
(2.4)

where, \( V \) is total volume in m\(^3\), \( N_A \) is the Avogadro constant (6.02214857\(^{23}/\)mol), \( n_i \) is the number of mole of ion \( i \).

The function \( \chi \) is given by:

\[ \chi(x) = \frac{3}{x^3} \left( \frac{3}{2} + \ln(1 + x) - 2(1 + x) + \frac{1}{2} (1 + x)^2 \right) \]  
(2.5)

This excess Helmholtz function only takes into account the non-ideality caused by the electrostatic interactions and does not account for non-ideality due to the short-range forces.

### 2.2 Born Equation

In the Debye-Hückel theory and related models, the interactions between ions and water are not described, thus the Debye-Hückel model cannot stand alone as a model for electrolyte solutions. In order to address this limitation, Stokes and Robinson put forward the theory of ionic hydration [30]. They stated that when ions are dissolved in solvent, the solvent molecules are polarized by the electrical charges.

The Born equation [26] can be used for estimating the electrostatic component of Gibbs free energy of solvation of an ion. It is an electrostatic model that treats the solvent as a continuous dielectric medium.

The molar change in free energy on transferring an ion from vacuum to a medium of dielectric constant [36] is expressed as:
\[ \Delta G = -\frac{Z_i^2 e^2}{8\pi\varepsilon_0 r_{\text{Born}}} \left[ 1 - \frac{1}{\varepsilon_r} \right] \] (2.6)

It is important to note that \( r_{\text{Born}} \) does not have, in principle, the same value as the ion diameter used in the ion-ion interaction calculation. It can be obtained from the above equation by writing it up for the case of an infinitely dilute electrolyte.

The excess chemical potential from ion hydration is defined as the difference in the solvation free energy of the concentrated and dilute solutions (the ion concentration is indicated as molarity ‘c’ [mol/L solution]):

\[ \mu_i^{EX,Born}(c) = \Delta G(c) - \Delta G(0) = \frac{Z_i^2 e^2}{8\pi\varepsilon_0 r_{\text{Born}}} \left[ \frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_w} \right] \] (2.7)

\( \varepsilon_w \) is the dielectric constant (relative static permittivity) of the solvent (water in this work).

### 2.3 Ion Association Theory

In the Debye-Hückel theory and the Born equation, the association between ions is not considered, and in polar solvent like water it is considered that the electrolyte is completely dissociated into ions. However, even with strong electrolytes, there is ion association in solvents with low dielectric constants.

Bjerrum [37] introduced the concept of ion association in order to improve the Debye-Huckel theory.

Ion association is a chemical reaction whereby ions of opposite electrical charge come together in solution to form a distinct chemical entity [38]. Ion associates are classified, according to the number of ions that associate with each other, as ion pairs, ion triplets, etc. There are three distinct types of ion pairs (contact, solvent-shared or solvent-separated), depending on the extent of solvation of the two ions [39].

The dielectric constant of the solvent is the most important factor to determine the extent of ion association.

Bjerrum [37] introduces a characteristic distance parameter \( q \).
When the distance between positive and negative ions is less than $q$, they will form an ion pair; when the distance between ions is greater than $q$, the positive and negative ions are free. The characteristic distance parameter $q$ is calculated as follows:

$$q = \frac{|Z_c Z_A| e^2}{8\pi \varepsilon_r kT}$$

However, in real solutions, the conversion from free ions to ion pairs is a gradual process, while Bjerrum treated it as a fixed value, so there is a certain assumption in the theory. In view of the shortcomings of the Bjerrum theory, some modifications and improvements have been made for the association theory [40, 41].

### 2.4 Extended version of Debye–Hückel

Some extensions and simplifications have been proposed for the Debye–Hückel theory in literature. Shilov and Lyashchenko [42] extended the Debye–Hückel theory to allow for an arbitrary concentration dependence of the electrolyte solution relative static permittivity.

The expression for the ion-ion interaction contribution to activity coefficient of ion is obtained as follows:

$$\ln \gamma_i = -\frac{Z_i^2 e^2 \kappa_0 \chi_1(\kappa_0, a)}{3kT\varepsilon_w} + \frac{\overline{V}_i \kappa_0^3 \sigma_1(\kappa_0, a)}{24\pi N_A}$$

where $\overline{V}_i$ is the partial molar volume of ion $i$, $a$ is the distance of closest approach which was assumed to be the sum of the radii, $a = r_{cation} + r_{anion}$. The mean partial molar volume of ions was estimated using the equation:

$$\overline{V}_i = \frac{4\pi N_A}{3} r_i^3$$

$\kappa_0$ is the usual inverse Debye length, defined with the use of static permittivity of solvent (with no salt):

$$\kappa_0^2 = \frac{4\pi e^2}{\varepsilon_w kT V} \sum_i n_i Z_i^2$$
where, \( n_i \) is the mole number of ion \( i \), \( V \) is the total volume of solution.

The function \( \chi_1 \) is expressed as:

\[
\chi_1(\kappa_0, a) = \tau_1(\kappa_0, a) + \frac{\sigma_1(\kappa_0, a)}{2} \tag{2.12}
\]

With the functions \( \tau_1(\kappa_0, a), \sigma_1(\kappa_0, a) \) being:

\[
\tau_1(\kappa_0, a) = 3 \int_0^1 \frac{\lambda^2}{f(\kappa_0 \lambda)(\sqrt{f(\kappa_0 \lambda) + \kappa_0 a \lambda})} d\lambda \tag{2.13}
\]

\[
\sigma_1(\kappa_0, a) = 3 \int_0^1 \frac{f(\kappa_0 \lambda)^{3/2} - \frac{3}{2} \sqrt{f(\kappa_0 \lambda)} f'(\kappa_0 \lambda) \kappa_0 \lambda - a f'(\kappa_0 \lambda) \kappa_0^2 \lambda^2}{f(\kappa_0 \lambda)^2(\sqrt{f(\kappa_0 \lambda) + \kappa_0 a \lambda})^2} \lambda^2 d\lambda \tag{2.14}
\]

The concentration dependence of the static permittivity is represented using the function \( f(\kappa_0) \) which is defined by:

\[
\varepsilon(\lambda) = \varepsilon_w f(\kappa_0 \lambda) \tag{2.15}
\]

The experimental concentration-dependent dielectric constant is given form the correlation equation:

\[
\varepsilon(c) = \varepsilon_w - \delta S c + b S c^{3/2} \tag{2.16}
\]

where \( \varepsilon_w = 78.45 \) is the dielectric constant of water (the infinite dilute solution) at \( T = 298.15 \) K. \( c \) is salt molarity (mol/L solution). More details can be found in the original publications [43, 44].

### 2.5 Mean Spherical Approximation (MSA)

Combining the statistical theory of the Ornstein-Zernike equation with the integral equation theory is the starting point of the MSA derivation. By solving the particle in the solution of a radial distribution function solution model, MSA [29] was proposed. The model treats ions as charged hard spheres, the solvent as a continuum, and the thermodynamic properties expression is obtained by solving the integral equation.

By using an average diameter of the ions in the solution, the MSA expression for the excess Helmholtz energy can be reduced to a simpler, explicit form [29]:
\[ A_{EX} = -\frac{2\Gamma_{MSA}^3 RTV}{3\pi N_A} \left(1 + \frac{3}{2} \Gamma_{MSA} \sigma\right) \]  

(2.17)

The average diameter \( \sigma \) is calculated using the diameters of ions \( \sigma_i \):

\[ \sigma = \frac{\sum_{i \text{ions}} n_i \sigma_i}{\sum_{i \text{ions}} n_i} \]  

(2.18)

\( \Gamma_{MSA} \) is given with an implicit expression:

\[ \Gamma_{MSA} = \frac{1}{2\sigma} \left[ \sqrt{1 + 2\sigma \kappa} - 1 \right] \]  

(2.19)

\( 1/\kappa \) is a characteristic length called the screening length, and is identical to the expression used in Debye-Hückel theory:

\[ \kappa = \left(\frac{e^2 N_A^2}{\varepsilon_r \varepsilon_0 RTV} \sum_{i \text{ions}} n_i Z_i^2\right)^{1/2} \]  

(2.20)

Here, \( \varepsilon_0 \) is the permittivity in vacuum (8.8542\( \cdot \)12 C\(^2\)/J/m).

### 2.6 Electrolyte Cubic Plus Association

The electrolyte equation of state is applicable to model complex electrolyte systems, especially useful at high pressures. In e-CPA, the residual Helmholtz energy is given by:

\[ A^r = A^{SRK} + A^{ASSOC} + A^{DH} + A^{Born} \]  

(2.21)

In the right-hand side of the above equation, the first two terms are the contributions from CPA, and the remaining two contributions are from the Debye-Hückel theory [13] (for the long-range interaction of the ions) and Born equation [26] (for ion solvation), respectively.

The residual Helmholtz energy for the cubic Soave–Redlich–Kwong EOS [45] is calculated from:

\[ A^{SRK} = nRT \left[ -\ln \left(1 - \frac{b}{v}\right) - \frac{a(T)}{bRT} \ln \left(1 + \frac{b}{v}\right) \right] \]  

(2.22)

where \( n \) is the total number of moles, \( T \) is the temperature, \( R \) is the gas constant, \( v \) is the molar volume, and \( b \) and \( a(T) \) are the
co-volume parameter and the temperature dependent energy parameter of the mixture, respectively.

\[ b = \sum_i x_i b_i \]  

(2.23)

where \( b_i \) is the pure co-volume parameter and \( x_i \) is the mole fraction of component \( i \) (solvent, gas, cation, anion).

For the binary system of water and gas, the classical one-fluid mixing rule is used for \( a(T) \).

\[ a(T) = \sum_i \sum_j x_i x_j \sqrt{a_i(T) a_j(T) (1 - k_{ij})} \]  

(2.24)

The temperature dependent component specific parameter \( a_i(T) \) is given by:

\[ a_i = a_{0i} \left( 1 + c_{1i} \left( 1 - \sqrt{T_{ri}} \right) \right)^2 \]  

(2.25)

where \( T_{ri} \) is the reduced temperature of component \( i \), defined as \( T_{ri} = T / T_{ci} \), \( T_{ci} \) is the critical temperature of component \( i \).

For the binary system involving an ion, the Huron-Vidal/NRTL (HV-NRTL) infinite pressure mixing rule is used, due to its additional flexibility for electrolyte systems [24, 46]:

\[ \frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{g_{E,\infty}}{\ln 2} \]  

(2.26)

\[ \frac{g_{E,\infty}}{RT} = \sum_i x_i \frac{\sum_j x_j b_j \exp \left( -\alpha_{ji} \frac{\Delta U_{ji}}{RT} \right) \Delta U_{ji}}{\sum_j x_j b_j \exp \left( -\alpha_{ji} \frac{\Delta U_{ji}}{RT} \right)} \]  

(2.27)

where \( g_{E,\infty} \) is the excess Gibbs energy at infinite pressure calculated with the NRTL equation, \( \alpha_{ji} \) is the NRTL non-randomness parameter, \( \Delta U_{ji} \) is the change in interaction energy between like and unlike interactions (\( \Delta U_{ji} = \Delta U_{ij} - \Delta U_{jj} \)).

It is worth pointing out that the HV-NRTL infinite pressure mixing rule has the flexibility to reduce to the classical one-fluid mixing rule if \( \alpha_{ji} \) is set to zero and \( \Delta U_{ji} \) is appropriately chosen.

In order to apply the model over a wide range of temperature, a quadratic temperature dependence for the interaction parameter was proposed [24]:
\[
\frac{\Delta U_{ij}}{R} = \frac{\Delta U_{ij}^{ref}}{R} + \omega_{\Delta U_{ij}} \left[ \left( 1 - \frac{T}{T_{\Delta U_{ij}}} \right)^2 - \left( 1 - \frac{T_{\text{ref}}}{T_{\Delta U_{ij}}} \right)^2 \right]
\]  
(2.28)

where \( \Delta U_{ij}^{ref} \) is a binary interaction parameter between ion and solvent/gas at the reference temperature, \( \omega_{\Delta U_{ij}} \) is an adjustable parameter for the linear dependency in the interaction energy calculation, \( T_{\Delta U_{ij}} \) is a parameter of the temperature dependency.

\( T_{\text{ref}} \) is the reference temperature at which \( \Delta U_{ij}^{ref} \) is valid, \( T_{\text{ref}} \) is set to 298.15 K in this work.

The residual Helmholtz energy for association \( A^{ASSOC} \) is based on the formulation of Wertheim’s association theory [47, 48] and can be found from the solution of the constrained optimization problem [49] given by:

\[
A^{assoc} = RT \left[ \sum_i n_i \sum_{A_i} \left( \ln X_{A_i} - \frac{1}{2} X_{A_i} + \frac{1}{2} \right) \right]
\]  
(2.29)

\[
\frac{1}{X_{A_i}} = 1 + \sum_j \rho_j \sum_{B_j} X_{B_j} \Delta_{A_iB_j}
\]  
(2.30)

where \( n_i \) is the number of moles of component \( i \), \( X_{A_i} \) is the fraction of site A on component \( i \) that is not bonded to any other site, \( \rho_j \) is the density of component \( j \), and \( \Delta_{A_iB_j} \) is the association strength, which is calculated from:

\[
\Delta_{A_iB_j} = g(\rho) \left[ \exp \left( \frac{\varepsilon_{A_iB_j}}{k_B T} \right) - 1 \right] b_{ij} \beta^{A_iB_j}
\]  
(2.31)

where the two association parameters are the association volume, \( \beta^{A_iB_j} \), and the association energy, \( \varepsilon^{A_iB_j} \), while \( b_{ij} \) is given by \( b_{ij} = \ldots \)
\((b_i + b_j)/2\). The simplified radial distribution function is expressed as: 
\[ g(\rho) = (1 - 1.9\eta)^{-1} \], and the packing fraction \(\eta\) is equal to \(b/4v\).

The contribution to the Helmholtz energy from the long-range interaction of the ions is calculated from the DH theory [13], as shown in the following equation:

\[
A_{DH} = -\frac{k_B T V_4}{4\pi NA \sum_i n_i Z_i^2} \sum_i n_i Z_i^2 \chi_i \tag{2.32}
\]

And the function \(\chi_i\) is given by:

\[
\chi_i = \frac{1}{d_i^3} \left[ \ln(1 + \kappa d_i) - \kappa d_i + \frac{1}{2} (\kappa d_i)^2 \right] \tag{2.33}
\]

where \(\kappa\) is the inverse Debye screening length, and \(d_i\) is the hard-sphere diameter of the ion.

Finally, the contribution of ion solvation comes from the Born equation [26, 50]:

\[
A_{Born} = \frac{N_A e^2}{8\pi \varepsilon_0} \sum_i n_i Z_i^2 \left( \frac{1}{\varepsilon_r} - 1 \right) \tag{2.34}
\]

where \(r_{Born,i}\) is the radius of the Born cavity caused by the transfer from vacuum to the fluid phase, and \(e\) is the elementary charge.

The relative static permittivity \(\varepsilon_r\) is of central importance in the thermodynamics of electrolyte solutions [51]. In e-CPA, the model developed by Maribo-Mogensen et al. [52] for the relative static permittivity is used in both the Debye-Hückel and Born terms.

Maribo-Mogensen et al. [24] introduced a Peneloux volume translation, as shown in Eq. (2.35), to improve the description of density of salt solutions with e-CPA

\[
v = v^{EoS} + \sum_{\text{all ions}} x_i C_i \tag{2.35}
\]

where \(v\) is the molar volume, \(v^{EoS}\) is the molar volume calculated from the e-CPA EOS, \(x_i\) is the mole fraction of ion \(i\), and \(C_i\) is the Peneloux volume correction parameter of ion \(i\).
The relative static permittivity depends on the thermodynamic state (the temperature and concentration of the electrolyte), in this work, concentration-dependent static permittivity is used in ion-ion interaction calculation and ion-water interaction calculation (Born term).
Chapter 3. Modeling of Aqueous Electrolyte Solutions

This chapter presents thermodynamic modeling for aqueous solutions of several quaternary ammonium salts (single-salt solutions), and metal halide salts (multi-salt solutions).

Most parts of this chapter are based on the 2 published manuscripts:


Chapter structure and contents:
3.1. Metal Halide Systems
3.2. Quaternary Ammonium Salt Systems
3.3. Discussion
3.4. Conclusion
Introduction

For some aqueous solutions of metal halide salts, the water molecules arrange around the ions, these water molecules are no longer freely available for the development of hydrogen bonds with other water molecules [3]. The presence of multi-salt will cause the solution more complex. The presence of QAS can form semi-clathrate hydrate (SCH), in the structure of SCH, the anions of salts coupled with water molecules build a clathrate framework and the cation is embedded in framework cavities, while the small guest gas molecules could be contained in empty pentagonal dodecahedron cages [6].

The thermodynamic modeling of aqueous solution is important for chemical industries, and it is the prerequisite work for vapor-liquid-hydrate modeling. Prior to modeling, the properties and pure component parameters should be proposed. Water is the solvent in this work, Table 3.1 lists the properties and parameters of water in e-CPA. Table 3.2 lists the ion radius and Born radius of ions.

The related properties and parameters of water and anions taken from literature [24, 25, 53, 54] are given in Tables 3.1 and 3.2. The anion radius used in this modeling work is the calculated ionic radius in solution from Marcus [54].

Table 3.1 Properties and parameters of water in e-CPA.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>values</th>
<th>Reference</th>
<th>Parameters</th>
<th>values</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma = \frac{a_0}{R_b}$ [K]</td>
<td>1017.34</td>
<td>[25, 53]</td>
<td>$\alpha_{0,i}$</td>
<td>1.613</td>
<td>[55]</td>
</tr>
<tr>
<td>$c_1$</td>
<td>0.6736</td>
<td>[25, 53]</td>
<td>$\mu_{0,i}$ [D]</td>
<td>1.855</td>
<td>[55]</td>
</tr>
<tr>
<td>$b$ [cm$^3$/mol]</td>
<td>14.515</td>
<td>[25, 53]</td>
<td>$\gamma$ [$^\circ$]</td>
<td>63.5</td>
<td>[56]</td>
</tr>
<tr>
<td>Association scheme</td>
<td>4C</td>
<td>[25, 53]</td>
<td>$\varphi$ [$^\circ$]</td>
<td>104.5</td>
<td>[56]</td>
</tr>
<tr>
<td>$1000 \times \beta^{AB}_i$</td>
<td>69.2</td>
<td>[25, 53]</td>
<td>$\theta$ [$^\circ$]</td>
<td>94.79</td>
<td>[56]</td>
</tr>
</tbody>
</table>
In Table 3.1, $T_c$ is the critical temperature, $a_0$ is the van der Waals attractive energy parameter of the mixture, $b$ is the CPA co-volume, $\Gamma$ is CPA reduced energy parameter ($a_0/Rb$), $c_i$ is the CPA parameter in the temperature dependency of the energy parameter. $\alpha_{0,i}$ is the molecular polarizability [$10^{-40} \text{C} \cdot \text{m}^2 \cdot \text{V}^{-1}$], $\beta_{Ai Bj}$ is association volume between site A on molecule $i$ and site B on molecule $j$, $\varepsilon_{Ai Bj}$ is association energy between site A on molecule $i$ and site B on molecule $j$, $\mu_0$ is the dipole moment of water in vacuum, $\gamma$ is the angle between the two dipole moments, $\phi$ is the internal C-O-H angle, and $\theta$ is the rotation angle between hydrogen bonds in different shells, ‘4C’ means four-site (4C) scheme.

Table 3.2 Ion properties and parameters (from literature).

<table>
<thead>
<tr>
<th>Ion</th>
<th>$r_p$ a [Å]</th>
<th>$r_{\text{Born}}$ b [Å]</th>
<th>$d$ c [Å]</th>
<th>$r_{\text{Born}}$ b [Å]</th>
<th>$b^d$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>0.95</td>
<td>1.62</td>
<td>2.36</td>
<td>1.665</td>
<td>16.49</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.33</td>
<td>1.95</td>
<td>2.78</td>
<td>2.065</td>
<td>27.62</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.99</td>
<td>1.71</td>
<td>2.42</td>
<td>1.759</td>
<td>17.91</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.65</td>
<td>1.42</td>
<td>2.09</td>
<td>1.443</td>
<td>11.51</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>1.05</td>
<td>1.96</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F$^-$</td>
<td>1.36</td>
<td>1.60</td>
<td>2.63</td>
<td>1.411</td>
<td>22.94</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1.81</td>
<td>2.26</td>
<td>3.19</td>
<td>1.828</td>
<td>40.83</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>1.95</td>
<td>2.47</td>
<td>3.37</td>
<td>2.059</td>
<td>48.40</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>-</td>
<td>-</td>
<td>3.82</td>
<td>2.415</td>
<td>70.03</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>-</td>
<td>-</td>
<td>3.58</td>
<td>2.04</td>
<td>39.80</td>
</tr>
</tbody>
</table>

a. Pauling radius; b. Born radius; c. hard-sphere diameter; d. CPA co-volume parameter.

In Chapter 3, Chapter 4 and 5.3.2 of Chapter 5, ion size from Marcus [54] and Born radii from our previous work [24] are used. In 5.3.1 of Chapter 5, Pauling radii [57] and Born radii from Valiskó et al. [44, 58] are used, for SO$_4^{2-}$ and NO$_3^-$, e-CPA parameters are used.
3.1 Metal Halide Systems

3.1.1 Single-salt Systems

Maribo-Mogensen et al. [24] have modeled several water+salt binary systems, and gave the interaction parameters between ions and water. The binary systems of \( \text{H}_2\text{O}+\text{NaCl}, \text{H}_2\text{O}+\text{KCl}, \text{H}_2\text{O}+\text{CaCl}_2, \text{H}_2\text{O}+\text{MgCl}_2, \) and \( \text{H}_2\text{O}+\text{Na}_2\text{SO}_4 \) have been investigated previously. The modelling performance of e-CPA on mean ionic activity coefficients and osmotic coefficients of these systems are shown in Figure 3.1. It is readily seen that e-CPA with the binary interaction parameters from literature [24] can correlate the mean ionic activity coefficients and osmotic coefficients for \( \text{H}_2\text{O}+\text{salt} \) binary systems very well.

It is worth mentioning that the mean ionic activity coefficients and osmotic coefficients of aqueous solutions of NaCl, KCl, CaCl\(_2\), MgCl\(_2\) and Na\(_2\)SO\(_4\) exhibit different trends. The activity coefficients for aqueous solutions of CaCl\(_2\) and MgCl\(_2\) decrease first and then increase sharply as the salt concentration increases. These properties of the aqueous solutions of Na\(_2\)SO\(_4\) are smaller than those of other systems. Table 3.3 shows the model performance for aqueous solutions of some metal halide salts.
Figure 3.1 Experimental and calculated mean ionic activity coefficients and osmotic coefficients for binary systems at 298.15 K: H$_2$O+NaCl [59]; H$_2$O+KCl [60]; H$_2$O+CaCl$_2$ [61]; H$_2$O+MgCl$_2$ [62], H$_2$O+Na$_2$SO$_4$ [63]. Dash lines are for mean ionic activity coefficients ($\gamma_m^\pm$) and solid lines are for osmotic coefficients ($\Phi$).

Table 3.3 Modelling performance of mean ionic activity coefficients and osmotic coefficients for water-ions (metal halide salts) binary systems [5].

<table>
<thead>
<tr>
<th>Salt</th>
<th>$^\Delta u_{ij}^{ref}$/R [K]</th>
<th>$T^\Delta U_{ij}$ [K]</th>
<th>$\omega^\Delta U_{ij}$ [K]</th>
<th>T [K]</th>
<th>$m_{max}^a$ [mol/kg]</th>
<th>RAD [%]$^c$</th>
<th>$\gamma_{m}^\pm$</th>
<th>$\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>-223.5</td>
<td>340</td>
<td>1573</td>
<td>273.15-473.15$^b$</td>
<td>7.973</td>
<td>2.3</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>-130.0</td>
<td>340</td>
<td>1361</td>
<td>273.15-373.15$^b$</td>
<td>6.0</td>
<td>0.86</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>-380.8</td>
<td>340</td>
<td>2778</td>
<td>298.15 $^b$</td>
<td>3.0</td>
<td>5.3</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>-459.6</td>
<td>340</td>
<td>2439</td>
<td>298.15 $^b$</td>
<td>3.0</td>
<td>5.9</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>123.8</td>
<td>300</td>
<td>1163</td>
<td>298.15-323.15$^b$</td>
<td>3.7</td>
<td>2.0</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>NaBr</td>
<td>-280.3</td>
<td>350</td>
<td>1322</td>
<td>246-523</td>
<td>6.0</td>
<td>7.6</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>NaF</td>
<td>-167.0</td>
<td>320</td>
<td>-2183</td>
<td>269-308</td>
<td>1.0</td>
<td>2.2</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>77.38</td>
<td>300</td>
<td>891.5</td>
<td>271-498</td>
<td>2.0</td>
<td>2.9</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>
In Table 3.3, $\Delta U_{ij}^{ref}$ is binary interaction parameter between cation/anion and solvent (or gas) at the reference temperature (Eq. (2.27) of Chapter 2), $\omega_{\Delta U_{ij}}$ is an adjustable parameter for the linear dependency in interaction energy calculation (Eq. (2.27) of Chapter 2), $T_{\Delta U_{ij}}$ is a parameter of the temperature dependency (Eq. (2.27) of Chapter 2), $\gamma_{\pm}^m$ is the mean ionic activity coefficients, $\phi$ is osmotic coefficients; a. In Maribo-Mogensen et al.’s work [24], the regression molality limits are: 6, 6, 3, 2 mol/kg water for NaCl, KCl, CaCl$_2$, MgCl$_2$, Na$_2$SO$_4$ respectively; b. Verification work, NaCl data source [59, 63-74], KCl data source:[60, 75-77], CaCl$_2$ data source:[61, 78], MgCl$_2$ data source: [62, 78], Na$_2$SO$_4$ data source: [79-82]. c. The results are typically listed as the relative average deviation (RAD):

$$
RAD\% = \frac{1}{N_p} \sum_{i}^{N_p} \left| \frac{y_i^{cal} - y_i^{exp}}{y_i^{exp}} \right| \times 100\% \tag{3.1}
$$

Here, $N_p$ is the number of data points, $y_i^{cal}$ represents the calculated results of any property, e.g. solubility, osmotic coefficient, or water activity, and $y_i^{exp}$ represents the experimental data of the given property.

### 3.1.2 Multi-salt Systems

In nature, most aqueous electrolyte solutions are multi-salt systems. In this part, several aqueous multi-salt solutions (H$_2$O+KCl+NaCl, H$_2$O+Na$_2$SO$_4$+NaCl, H$_2$O+NaCl+KCl+MgCl$_2$) will be studied.

Within the e-CPA framework, there are no binary interaction parameters between ions, and the parameters for H$_2$O+single salt can be applied to multi-salt solutions without new adjustable parameters, provided that the anion and cations are compatible (having the same cation or same anion).

Table 3.4 lists the predictions of the osmotic coefficients and water activity for aqueous multi-salt solutions. It can be seen from Table
3.4 that e-CPA can give good agreement with water activity and osmotic coefficients of aqueous multi-salt solutions, except for the system H$_2$O+CaCl$_2$+MgCl$_2$. The large deviation of H$_2$O+CaCl$_2$+MgCl$_2$ is because the salt molality goes far beyond the correlation range, or saying the maximum effective molality range, and the ion-pairing effect may have become an important contribution, which is not considered in e-CPA.

Table 3.4 e-CPA performance for aqueous multi-salt solutions.

<table>
<thead>
<tr>
<th>Salts</th>
<th>T [K]</th>
<th>$I_{\text{max}}$</th>
<th>$N_p$</th>
<th>RAD [%]</th>
<th>$\phi$</th>
<th>$a_W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl+KCl</td>
<td>298.15</td>
<td>6 [83, 84]</td>
<td>57</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>KCl+CaCl$_2$</td>
<td>298.15</td>
<td>7.3 [85]</td>
<td>1</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CaCl$_2$+MgCl$_2$</td>
<td>298.15-323.15</td>
<td>11.334 [87]</td>
<td>71</td>
<td>9.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaCl+KCl+MgCl$_2$</td>
<td>298.15</td>
<td>8.714 [85]</td>
<td>2</td>
<td>2.7</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

In Table 3.4, $N_p$ is the number of data points, $\phi$ is osmotic coefficients and $a_W$ is water activity; +. $I_{\text{max}}$ is the maximum ionic strength [mol/kg water].

It can be concluded that the model with single cation/anion-H$_2$O interaction parameters can be used for aqueous multi-salt solutions directly.

### 3.2 Quaternary Ammonium Salt Systems

SCH have attracted attention in recent years, because of application possibilities such as gas separation, thermal storage, CO$_2$ sequestration and CH$_4$ transportation [6].

The special structure makes SCH more stable than usual hydrates. Since there is a wide range of anions and cations that can compose semi-clathrates, many different crystalline structures can be formed. QAS are common additives for SCH, and aqueous TBAX solutions have been extensively studied because of potential
industrial applications, such as intermediate reactants and as phase transfer catalysts [21]. Nowadays, TBAX (with X being bromide: B, chloride: C, fluoride: F, nitrate: NO3 etc.) and Tetra-n-butyl phosphonium halides (in short, TBPX) receive most attention as SCH additives [88-91]. Some other QAS (Tetra-n-methyl ammonium bromide: TMAB, Tetra-n-ethyl ammonium bromide: TEAB, Tetra-n-propyl ammonium bromide: TPAB) are also studied as additives for hydrate formation [92-94].

Table 3.5 summarize experimental studies of mean ionic activity coefficients and osmotic coefficients for TBAX aqueous solutions at atmospheric pressure. Different approaches have been proposed for TBAX aqueous solutions. One typical approach is the so-called $\varphi - \varphi$ approach, which uses an electrolyte EOS for all phases. Paricaud [21] used the statistical associating fluid theory with variable range for electrolytes (SAFT-VRE) to describe the fluid phases. Following Paricaud’s approach, Fukumoto et al. [95-97] adjusted the temperature dependency parameter in the SAFT-VRE EOS by using solid-liquid equilibrium data of salt+water binary systems, and applied the approach to TBAB, TBAC, TBAF, TBPB, and TBANO$_3$ SCH systems. Babu et al. [95] re-adjusted the depth of the square-well cell potential, enthalpic and melting point parameters. The SAFT-VRE EOS is shown to give a satisfactory agreement with experimental data for the mean ionic activity coefficients and osmotic coefficients of TBAX aqueous solutions [21, 96]. For other TBAX systems, Fukumoto et al. [96] stated that good description of mean ionic activity coefficients and osmotic coefficients of electrolyte solution can be obtained by using SAFT-VRE. Ma et al. [98] applied the Modified Patel-Teja (MPT) EOS [19] to the fluid phase equilibrium calculations for the TBAB aqueous solution and TBAF aqueous solution. The MPT EOS uses a Debye-Hückel term for the electrostatic contributions, while the authors [98] give few details of fluid modeling performance for TBAX related systems.
Another typical approach is the so-called $\varphi - \gamma$ approach, which uses a non-electrolyte EOS for the vapor phase and an electrolyte activity coefficient model for the liquid phase. The e-NRTL model proposed by Chen et al. [15] is a common model for the activity coefficient in this approach. e-NRTL performs very well in modeling activity coefficients of quaternary ammonium salts in water at 298.15 K [99]. Based on the mean spherical approximation for aqueous electrolytes (MSA-NRTL) model, AMSA-NRTL [100] takes the ionic hydration and association into account. Kwaterski and Herri [101] used the SRK EOS plus e-NRTL for the TBAB aqueous solution. Verrett et al. [102] used the Trebble–Bishnoi (TB) EOS plus e-NRTL for the TBAB aqueous solution, Shi and Liang [103] applied the Peng–Robinson (PR) EOS plus e-NRTL for TBAB, TBAC, and TBAF aqueous solutions, Najibi et al. [104] utilized the PR EOS plus AMSA-NRTL for TBAB aqueous solutions. Both e-NRTL and AMSA-NRTL provide good agreement with experimental data of mean ionic activity coefficients (the performance can be seen in the discussion section). Eslamimanesh et al. [105] used the PR EOS for the vapor phase, plus NRTL for non-electrolyte compounds in the liquid phase, and they used a correlation based on the experimental data for the mean ionic activity coefficients of the electrolyte part. These authors did not investigate the predictive ability of the model for TBAB related fluid systems. Other researchers [106-108] applied non-electrolyte EOS plus empirical correlations for water activity.

In this work, the e-CPA EOS proposed by Maribo-Mogensen et al. [24] is used. The adjustable parameters will be obtained by fitting the mean ionic activity coefficients and osmotic coefficients, and other thermodynamic properties will also be predicted by e-CPA. The parameter estimation procedure and modeling approaches will be analyzed and discussed.
Table 3.5 Experimental studies of mean ionic activity coefficients and osmotic coefficients for aqueous QAS solutions at atmospheric pressure.

<table>
<thead>
<tr>
<th>TBAX</th>
<th>m a</th>
<th>T b</th>
<th>Np*</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBAB</td>
<td>0.0912-1.0060</td>
<td>298.15</td>
<td>10</td>
<td>[110]</td>
</tr>
<tr>
<td></td>
<td>0.1-9.5</td>
<td>298.15, 373.15, 423.15</td>
<td>27+</td>
<td>[111]</td>
</tr>
<tr>
<td>TBAC</td>
<td>0.1-15</td>
<td>298.15</td>
<td>32</td>
<td>[109]</td>
</tr>
<tr>
<td>TBAF</td>
<td>0.1-1.6</td>
<td>298.15</td>
<td>13</td>
<td>[112]</td>
</tr>
<tr>
<td>TMAB</td>
<td>0.01285-5.5</td>
<td>298.15, 308.15</td>
<td>34</td>
<td>[109, 113]</td>
</tr>
<tr>
<td>TEAB</td>
<td>0.00966-6.0</td>
<td>298.15, 308.15</td>
<td>35</td>
<td>[109, 113]</td>
</tr>
<tr>
<td>TPAB</td>
<td>0.00795-6.0</td>
<td>298.15, 308.15</td>
<td>36</td>
<td>[109, 113]</td>
</tr>
</tbody>
</table>

a. Molality [mol/kg water]; b. Temperature [K]; * Np is the number of data points; + The authors gave the changes in osmotic coefficients and activity coefficients.

Figure 3.2 Molecular structures of QAS. [www.sigmaaldrich.com]
Quaternary ammonium cations ($R_4N^+$) are hydrophobic organic cations. It can be seen from Figure 3.2 that $R_4N^+$ has four long and soft hydrophobic alkyl side chains. The positive charge, which comes from the center nitrogen atom, is sterically hindered by the alkyl substituents. Thermodynamic properties of the aqueous QAS solutions are influenced by the interactions that occur between the hydrophobic alkyl groups of the ions and the water molecules [114].

Ion radius is a very important physical parameter in electrostatic calculations. Pauling [57] stated that there is no specified size which can be assigned to an ion, because of the indefinite extent of the electron distribution function. Pauling [57] also pointed that the apparent ionic radius will depend on the physical properties.

A typical study object is TBA$^+$, different type of ion sizes for TBA$^+$ are published. Pauling radius is calculated from the nuclear charge and the shielding constant based on Pauling rules. van der Waals radius is the radius of an imaginary hard sphere representing the distance of closest approach for another atom. Hard-sphere radius is calculated from the rigid sphere model. Hydrated radius is the radius of ion and closely bounded water molecules. Stokes radius (or hydrodynamic radius) is the radius of a hard sphere that diffuses at the same rate as the solute. McGowan radius is calculated from the McGowan characteristic volume, which is the actual volume of a mole when the molecules are not in motion.

Table 3.6 summarizes some published ion size of TBA$^+$, from which it can be seen that the radii of TBA$^+$ vary from 3.81 Å to 4.94 Å, a difference (highest to lowest value) of 1.13 Å. The TBA$^+$ is a soft and irregular organic cation, and it is not entirely clear which radius approximately reflects the physics of the electrostatic interactions. For this reason, the effect of ion radius on the thermodynamic modeling will be investigated in this work.
Table 3.6 Summary of literature values proposed for the radius of TBA$^+$. 

<table>
<thead>
<tr>
<th>Size Type</th>
<th>r [Å]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pauling crystal radius</td>
<td>4.94</td>
<td>[80]</td>
</tr>
<tr>
<td>van der Waals radius</td>
<td>3.87</td>
<td>[115]</td>
</tr>
<tr>
<td></td>
<td>4.13</td>
<td>[114, 116]</td>
</tr>
<tr>
<td>hard-sphere radius</td>
<td>3.81</td>
<td>[117]</td>
</tr>
<tr>
<td>hydrated radius</td>
<td>4.94</td>
<td>[118]</td>
</tr>
<tr>
<td></td>
<td>3.84</td>
<td>[119]</td>
</tr>
<tr>
<td>hydrodynamic radius</td>
<td>4.73</td>
<td>[120]</td>
</tr>
<tr>
<td></td>
<td>4.72</td>
<td>[80]</td>
</tr>
<tr>
<td>McGowan radius</td>
<td>4.62</td>
<td>[121]</td>
</tr>
</tbody>
</table>

3.2.1 Hydrophobic Effects

The hydrophobic effect causes the aggregation of hydrophobic groups in the presence of water or other polar solvents [122, 123]. The segregation of water and hydrophobic groups maximizes hydrogen bonding between molecules of water, and minimizes the area of contact between hydrophobic groups and water. Water may play an important role in the process of hydrophobic effects, because the strength of hydrogen bonding in water is stronger than that of van der Waals interaction. Interface will appear between the solute and water when hydrophobic effect occurs [124]. QAS is a favorite class of model substances for the investigation of hydrophobic effect [125]. By infrared, Stangret and Gampe [126] found that the average number of hydrogen bonds is significantly increased in TBA$^+$ aqueous solution. Hydrophobic effect might affect the thermodynamic properties of TBAX aqueous solutions, unfortunately, the origin of the hydrophobic effect is not fully understood, and the basic molecular processes are not well understood yet.

Cavell [127] measured dielectric constants of solutions of TBAB in acetone at 25°C, and found that the dielectric constant increases with increasing concentration. Buchner et al. [128] measured the complex permittivity of aqueous tetra-n-alkyl ammonium halide
solutions in the frequency range 0.2-89 GHz and fitted the data to Cole–Cole equation and Debye equation. They turned out that for the spectra of Pr$_4$NBr, Bu$_4$NBr, and Pe$_4$NBr, a fit with a sum of four Debye equations (4D model) is required. From Buchner et al.’s empirical equation [128], the relative static permittivity of TBAB aqueous solutions decreases with increasing solute molar concentration at the lower concentration range, but it increases with increasing solute mole concentration at the higher concentration range.

For the unusual behavior of the relative static permittivity of the aqueous TBAB solutions, Buchner et al. [128] commented that there is an additional dispersion step emerging for TBAB aqueous solution, because of the hydrophobic hydration, the ‘slow’ water is reduced and the average number of hydrogen bonds is increased. Kaatze [129] has also stated that the relative static permittivity values of the solutions may result from two opposite effects: enhancement of the water permittivity around the ions by the hydrophobic effect and reduction by kinetic polarization. An enhancement of the relative static permittivity reflects the incensement of short-range molecular interactions of the solvent around the hydrophobic particles.

If these assumptions are valid, there are three factors that affect the relative static permittivity: dielectric saturation and the kinetic depolarization which both contribute to the decrease of the relative static permittivity, the hydrophobic hydration contribution to the increase of the relative static permittivity.

### 3.2.2 Parametrization

As presented above, the framework of e-CPA is set up to account for each ion separately, and is by nature ion specific. The pure component e-CPA parameters of an ion are: co-volume parameter ($b_i$), reduced energy parameter ($T_i = a_{0i}/Rb_i$), pure component temperature dependence parameter for Soave's $\alpha(T)$-function ($c_{1i}$), association energy between site A on molecule $i$ and site B on
molecule \( j (e^{A_iB_i}) \), association volume between site A on molecule \( i \) and site B on molecule \( j (\beta^{A_iB_i}) \), hard-sphere diameter of ion \( (d_i) \) and Born radius of the ion \( (r_{\text{Born},i}) \). The binary interaction parameters of ions with water or gas are: NRTL non-randomness parameter \( (\alpha_{ji}) \), interaction parameter at the reference temperature \( (\Delta U_{ij}^{\text{ref}}) \), two adjustable parameters of the temperature dependency \( (\omega_{\Delta U_{ij}} \text{ and } T_{\Delta U_{ij}}) \). In order to minimize the number of parameters, some assumptions are made [24]: the temperature dependence parameter \( (c_{1i} \text{ in Eq. (2.25) of Chapter 2}) \), CPA reduced energy parameter \( (\Upsilon_i') \) of ions are set to zero; the ions are assumed to be non-associating, thus eliminating the two ion association parameters; the three size parameters \( b_i, d_i \) and \( r_{\text{Born},i} \) are connected with only one adjustable parameter left [27]. the NRTL non-randomness factor and the ion-ion interaction parameters are set to zero.

In this work, ion-solvent and ion-gas interaction parameters are transformed to cation/anion-solvent, and cation/anion-gas interaction parameters, which means that interaction parameters \( \Delta U_{\text{cation-solvent}} \) is equal to \( \Delta U_{\text{anion-solvent}}, \Delta U_{\text{cation-gas}} \) is equal to \( \Delta U_{\text{anion-gas}} \).

It is also assumed that the Born radius may be estimated by using the following empirical equations, which were first proposed by Latimer et al. [130] and later supported by molecular simulation [131]

\[
\begin{align*}
 r_{\text{Born,anion}} &= r_{\text{anion}} + 0.1 \text{ Å} \quad (3.2) \\
 r_{\text{Born,cation}} &= r_{\text{cation}} + 0.85 \text{ Å} \quad (3.3)
\end{align*}
\]

In Eqs. (3.2) and (3.3), \( r_{\text{cation}} \) and \( r_{\text{anion}} \) are the hard-sphere radii of cation and anion, respectively, which are equal to half of the ion diameters \( (r_i = d_i/2, \text{ the '}d_i\text{' is the same value used in Eq. (2.33))} \). \( r_{\text{Born,cation}} \) and \( r_{\text{Born,anion}} \) are the Born radii of cation and anion, respectively.
For simple monatomic ions such as Na\(^+\) and Cl\(^-\) which can be assumed to be spherical, it is expected that the CPA co-volume parameter can be predicted to fair accuracy using the following equation [25]

\[
b = \frac{2}{3\pi N_A (2r_i)^3}
\]

(3.4)

Where \( r_i \) is the hard-sphere radius of the ion \( i \).

In this work, we treat the cations of QAS using the same approach. As mentioned earlier, the R\(_4\)N\(^+\) is a relatively large, irregular organic cation with soft alkyl chains, and the negative charge is provided by the nitrogen atom. It is unclear which radius value reflects the physical facts more accurately.

In this work, the same TBA\(^+\) ion radius is used for aqueous solutions of TBAX. Since the TBAB aqueous solution is the most widely studied system, and the one for which most experimental data is available, the TBA\(^+\) ion radius is obtained by fitting the TBAB aqueous solution data.

TMA\(^+\), TEA\(^+\), TPA\(^+\) are also soft and irregular organic. Radii of these three R\(_4\)N\(^+\) will also be obtained by fitting mean ionic activity coefficients and osmotic coefficients of aqueous solutions of TMAB, TEAB, TPAB respectively.

In regression works, the objective function used for the regression is:

\[
F = \sum \left[ \frac{x_i^{cal} - x_i^{exp}}{x_i^{exp}} \right]^2
\]

(3.5)

Where \( x_i^{cal} \) represents the calculated values (mean ionic activity coefficients and osmotic coefficients), and \( x_i^{exp} \) represents the experimental values.

The fitted parameters are presented in Table 3.7.

The temperature dependency \( T_{\Delta U_{ij}} \) was respectively set to 350 K, 340 K and 300K for bromine salts, chloride salts and sulfate salts in the work of Maribo-Mogensen at el [56]. In this work, three fitting approaches have been investigated for the regression of the
ion-gas binary interaction parameters, as listed in Table 3.8. Approach A has 3 adjustable parameters (including 2 temperature-dependent parameters), Approach B has 2 adjustable parameters (including 1 temperature-dependent parameter), and Approach C has 1 adjustable parameter (no temperature-dependent parameters).

Table 3.7 e-CPA parameters for R₄N⁺.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma ) [K]</td>
<td>Set to 0</td>
</tr>
<tr>
<td>( c_1 )</td>
<td>Set to 0</td>
</tr>
<tr>
<td>( b ) [cm³/mol]</td>
<td>Calculated from cation radius</td>
</tr>
<tr>
<td>( \beta_{A_iB_j} )</td>
<td>Set to 0</td>
</tr>
<tr>
<td>( \varepsilon_{A_iB_j}/R ) [K]</td>
<td>Set to 0</td>
</tr>
</tbody>
</table>

* The Born radius \( r_{Born,i} \) of cation is calculated from ion radius by using Eq. (3.3), the Born radius of anion is calculated from ion radius by using Eq. (3.2), the CPA co-volume \( b \) is calculated from ion radius by using Eq. (3.4).

Table 3.8 Fitting approaches of ion-molecular interaction parameters used.

<table>
<thead>
<tr>
<th>Approach</th>
<th>( \Delta U_{ij}^{ref}/R ) [K]</th>
<th>( T_{\Delta U_{ij}} ) [K]</th>
<th>( \omega_{\Delta U_{ij}} ) [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>adjustable</td>
<td>adjustable</td>
<td>adjustable</td>
</tr>
<tr>
<td></td>
<td></td>
<td>340 K (for chloride salts)</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>adjustable</td>
<td>300 K (for sulfate salts)</td>
<td>adjustable</td>
</tr>
<tr>
<td></td>
<td></td>
<td>350 K (for bromine salts)</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>adjustable</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

In this Chapter, the temperature-range of activity coefficients for aqueous solutions of TMAB, TEAB, TPAB, TBAB are wide, so, we apply Approach A for aqueous solutions of TMAB, TEAB, TPAB, TBAB. In Chapter 4, three approaches will be studied.
3.2.3 Modeling Results

The regressed value of the TBA$^+$ radius $r$ is 2.25 Å, which is smaller than 3.81 Å [117], and larger than the value of N$_3^-$ (1.46 Å) [55]. Paricaud [21] reported the molecular radius of 1.927 Å for TBAB, and Ma et al. [19] obtained the ion radius of 1.4555 Å for TBA$^+$. These researchers presented smaller radius of TBA$^+$, one reason being that they did not take the Born term into account which may indicate that they incorporate the hydration effect into the long-range interaction. Moreover, it may indicate that all these electrolyte EOS might have not fully captured the physics of the TBAX aqueous solutions. From Table 3.9, it can be seen that the ion radii of TMA$^+$, TEA$^+$, TPA$^+$ are smaller than the published effective radii (TMA$^+$: 2.51 Å, TEA$^+$: 3.08 Å, TPA$^+$: 3.49 Å) [117]. The order of regressed radii of TMA$^+$, TEA$^+$ and TPA$^+$ is consistent with the values of the published effective radii. The difference between regressed value and published radii values is mainly because of the structure of the cations; the hydrocarbon chains are long and soft and the positive charge comes from the centre nitrogen atom.

It can be also seen from Table 3.9 that the absolute values of interaction parameters between water and ions $\Delta U_{ij}^{ref}$ at reference temperature also follow a decreasing sequence: TBAF>TBAC>TBAB>TPAB>TEAB>TMAB, and the order is according to the size of anion (TBAF, TBAC and TBAB), and the length of the hydrocarbon chains (TBAB, TPAB, TEAB and TMAB).

Firstly, the data of TBAX are shown and discussed. It can be seen from Figure 3.3 that these two properties of TBAX aqueous solutions are complex functions of molality. For the TBAB system, at low to medium salt concentration, both the mean ionic activity coefficients and osmotic coefficients decrease with increasing salt concentration. At higher salt concentration, both activity coefficients show a slight increase. For the TBAC system, at low
molality, the values of mean ionic activity coefficients and osmotic coefficients first decrease, and then increase to reach maxima at around 2 mol/kg water. After the maxima, the values first decrease, and then rise again. The mean ionic activity coefficients and osmotic coefficients of TBAF solution increase sharply with increasing salt concentration. Wen et al. [112] stated that the large values for these fluorides could be attributed to the ‘structural repulsion’: F\(^-\) anion is small and may tend to immobilize water in a more or less radial pattern around it due to its specific size and surface charge density [112]. The TBA\(^+\) is large and tends to enhance the ‘cage-like’ structure of water due to its hydrophobic properties. The cation and anion compete against each other to influence the structure of water in different ways.

Table 3.9 Binary ion-water interaction parameters and model performance.

<table>
<thead>
<tr>
<th>Salt</th>
<th>( r_{\text{cation}} ) ( [\text{Å}] )</th>
<th>( \Delta U_{ij}^{r\text{ef}} / R ) [K]</th>
<th>( T_{\omega U_{ij}} ) [K]</th>
<th>( \omega_{\Delta U_{ij}} ) [K]</th>
<th>( T ) [K]</th>
<th>( m )</th>
<th>RAD [%]</th>
<th>( \gamma_{m}^{\pm} )</th>
<th>( \phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMAB</td>
<td>1.75</td>
<td>-0.70</td>
<td>61.5</td>
<td>-73.1</td>
<td>298.15-308.15</td>
<td>5.5</td>
<td>3.0</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>TEAB</td>
<td>2.11</td>
<td>-24.42</td>
<td>622.2</td>
<td>570.9</td>
<td>298.15-308.15</td>
<td>6.0</td>
<td>4.7</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>TPAB</td>
<td>2.23</td>
<td>-41.77</td>
<td>950</td>
<td>331</td>
<td>298.15-308.15</td>
<td>6.0</td>
<td>4.4</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>TBAB</td>
<td>2.25</td>
<td>-114.9</td>
<td>192.4</td>
<td>137.3</td>
<td>298.15-373.15</td>
<td>10.0</td>
<td>7.2</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>TBAC</td>
<td>2.25</td>
<td>-219.3</td>
<td>-</td>
<td>-</td>
<td>298.15</td>
<td>10.0</td>
<td>6.6</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>TBAF</td>
<td>2.25</td>
<td>-450.1</td>
<td>-</td>
<td>-</td>
<td>298.15</td>
<td>1.6</td>
<td>4.8</td>
<td>2.6</td>
<td></td>
</tr>
</tbody>
</table>

a. \( r_{\text{cation}} \) is ion radius of cation; b. molality [mol/kg water]; c. The values are obtained by fitting experimental data of mean ionic activity coefficients and osmotic coefficients: TBAB data source: [109-111], TBAC data source: [109], TBAF data source: [112], TMAB data source: [109, 113], TEAB data source: [109, 113], TPAB data source: [109, 113].

Figure 3.3 presents the results of mean ionic activity coefficients and osmotic coefficients of TBAX aqueous solutions. It can be seen that, at the same molality, the order of values of osmotic coefficients and mean ionic activity coefficients are: TBAF > TBAC >
TBAB. Combining this with pure component parameters and the parameters of Table 3.9, we observe that the order of the absolute value of the interaction parameter $\Delta U_{ij}^{ref}$ follows the opposite order of halide ion size. This can be explained by the fact that the smaller the radius of the halide ion is, the larger interaction with water molecules is expected.

Figure 3.3 Calculated mean ionic activity coefficients and osmotic coefficients of TBAB, TBAC and TBAF aqueous solutions at 298.15 K using the e-CPA EOS against experimental data [109, 110, 132]).

Figure 3.4 shows the model performance of mean ionic activity coefficients and osmotic coefficients for the aqueous solutions of TPAB, TEAB and TMAB.
Figure 3.4 Experimental and calculated mean ionic activity coefficients and osmotic coefficients for binary systems at 298.15 K: H$_2$O+TMAB [109]; H$_2$O+TEAB [109]; H$_2$O+TPAB [109].

From Figure 3.4, it can be seen that e-CPA can reasonably correlate the mean ionic activity coefficients from a quantitative point of view. For the osmotic coefficients of TEAB+H$_2$O and TPAB+H$_2$O systems, the deviations between calculated and experimental values are relatively large at moderate salt concentrations (molality>2.0 mol/kg water), with the deviations following a decreasing sequence: TPAB>TEAB>TMAB, which links to the length of hydrocarbon chains of cations, and the deviations may be attributed to the hydrophobic effects caused from hydrocarbon chains [27].

It can be seen from above that e-CPA can give reasonably good results for the mean ionic activity coefficients and osmotic coefficients of aqueous QAS solutions. We conclude that the interaction parameters between ions and water can be used for modelling ternary systems, and we also believe that the hydrocarbon chain plays an important role on the phase behaviour of aqueous QAS solutions.
3.2.4 Prediction of Other Properties

Volumetric properties are important thermodynamic properties. Unfortunately, only aqueous TBAB solution volumetric data are available [133-136], and the molality range of the data is not as extended as those of the mean ionic activity coefficients and osmotic coefficients. Few saturation pressure data for aqueous solutions are available and only for TBAB aqueous solution [137]. The liquid density experimental data [133-136] are only available for the aqueous TBAB solution with the molality lower than 3.1 mol/kg water. The modeling results are shown in Figure 3.5, and it can be seen that e-CPA overestimates the liquid densities of TBAB solution, which may be because the model cannot represent the formation of low-density ice-like structures around the large hydrophobic TBA$^+$ [21].

The solid lines in Figure 3.5 show that e-CPA can give good agreement with experimental liquid density (RAD=0.2%) when using the Peneloux parameter of ions $C_i = 45.2$ cm$^3$/mol.

In addition to the calculations of activity coefficients and density, saturation pressure calculations are also important for thermodynamic modeling. Before calculating the saturation pressure of TBAB aqueous solution, the model was first used to predict the saturation pressure of NaCl solution under different molality and temperature conditions. The number of experimental data points [70, 138-140] is 327, the molality range is 0.5-7.2 mol/kg water, and the temperature range is 273.16-423.15 K. Excellent results are obtained for NaCl aqueous solution, as seen in Figure 3.6 (a). The RAD from the experimental data is 2.0%. It can be assumed that e-CPA can satisfactorily predict saturation pressure for single electrolyte systems.
Figure 3.5 Liquid densities of TBAB solutions at different temperatures from the e-CPA EOS (with parameters in Table 3.9) with and without using a Peneloux parameter against experimental data from Belandria et al. [134].

When e-CPA is used for TBAB aqueous solution, much larger deviations are observed, with RAD=7.1% and 5.4% at the two temperatures, as presented in Figure 3.6 (b), which also shows the estimated saturation pressure from the experimental osmotic coefficients

\[ P = P_w^{sat} a_w \]  \hspace{1cm} (3.6)

Where \( P \) is the saturation pressure of the system, \( P_w^{sat} \) is the saturation pressure of pure water the same temperature, and \( a_w \) is the activity of water, calculable from the experimental osmotic coefficient. In this equation, it is assumed that TBAB does not exist in the vapor phase, and it is a strong salt. It can be readily seen that the saturation pressure estimated from experimental osmotic coefficients match the prediction results of e-CPA very well.
Figure 3.6 (a) Predicted saturation pressure of NaCl aqueous solution for 353.15 K and 363.15 K from the e-CPA EOS against experimental data [140]; (b) Saturation pressure of TBAB aqueous solution from e-CPA and experimental osmotic coefficients, and saturation pressure of NaCl aqueous solution from e-CPA, both at 298.15 K. Experimental data are taken from Kurzin et al. [137], and Zhang et al. [138].
In order to further investigate how organic salts perform in terms of saturation pressure, the experimental data of some organic salts aqueous solutions [141-143] are collected and analyzed, which are plotted in the Figure 3.7. By comparing with saturation pressure data of TBAB aqueous solution, we can see that the saturation pressures of most salt aqueous solutions (including another Tetra-n-butyl ammonium salt aqueous TBANO₃ solution) are close to the values of NaCl aqueous solution in the given molality range, while TBAB aqueous solutions show very different saturation pressure values. Therefore, more systematic measurements for the saturation vapor pressure are needed.

Figure 3.7 Saturation pressure of aqueous organic salt solutions at 298.15 K. Benzyltri butyl ammonium Chloride (BTBAC) [141], TBANO₃ [141], Benzyltri methyl ammonium Chloride (BTMAC) [142], Benzytri ethyl ammonium Chloride (BTAC) [142], Benzyltri butyl ammonium Chloride (BTEAC) [142], Triethyl ammonium Chloride (CPTA) [143], 2-Hydroxy ethyl ammonium Chloride (2-HEAC) [143], Tris(hydroxymethyl) aminomethane Hydrochloride (THAMHC) [143], TBAB [137], NaCl [138].
3.3 Discussion

3.3.1 Analysis of Modeling of Relative Static Permittivity

The relative static permittivity is of central importance in the thermodynamics of electrolyte solutions [144, 145]. Many electrostatic permittivity theories or models represent or simulate the physical or thermodynamic properties of electrolyte solutions with the assumption that the solvent may be described as a dielectric continuum.

In e-CPA, the relative static permittivity is used in both Debye–Hückel and Born terms. Maribo-Mogensen et al. [24, 52, 56] presented a new model, where the relative static permittivity is calculated from an extension of the framework developed by Onsager, Kirkwood, and Fröhlich [146-148] to associating mixtures. The Wertheim’s association model is used to account for hydrogen bonding molecules and ion–solvent association (the ion–dipole association is due to electrostatic forces). According to Maribo-Mogensen et al. [24, 52, 56], the relative static permittivity in this work is obtained from:

\[
\frac{(2\varepsilon_r + \varepsilon_\infty)(\varepsilon_r - \varepsilon_\infty)}{\varepsilon_r} = \left(\frac{\varepsilon_\infty + 2}{3}\right)^2 \frac{N_A}{\varepsilon_0 k_B T \nu} \sum_i x_i g_i \mu_{i,0}^2 \tag{3.7}
\]

where \( \mu_{i,0} \) is the dipole moment of component \( i \) in vacuum, \( x_i \) is mole fraction of molecule \( i \), \( \varepsilon_0 \) is the vacuum permittivity.

The infinite frequency permittivity \( \varepsilon_\infty \) is obtained from the Clausius–Mossotti equation [149, 150]:

\[
\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{1}{3\varepsilon_0 \nu} \sum_i x_i \alpha_{0,i} \tag{3.8}
\]

where \( \alpha_{0,i} \) is the molecular polarizability of molecule or ion \( i \).

Finally, the Kirkwood g-factor [147, 151] is obtained from:
where $Z_{ij}$ is the coordination number of molecule $j$ around a central molecule $i$, $P_{ij}$ is the probability that molecule $i$ is associated to molecule $j$ (determined from solution to the site fractions $X_{A_j}$), $P_i = \sum_{j \in S} P_{ij}$ is the probability of the molecule $i$ to be bonded to any of the molecules in the setting, $\gamma_{ij}$ corresponds to the angle between the dipole moments of molecule $i$ and $j$ in the hydrogen bond network, and $\theta_{ij}$ is the rotation angle between hydrogen bonds in different shells. For more details and parameter values, refer to Maribo-Mogensen et al.’s work [52].

Firstly, the calculation of the relative static permittivity of aqueous NaCl solution with e-CPA parameters is performed in Figure 3.8. It shows on one hand that e-CPA qualitatively capture the relationship between the relative static permittivity and salt concentration, i.e. the relative static permittivity decreases significantly with increasing salt concentration. On the other hand, e-CPA overestimates the relative static permittivity values, which we believe is because, as a thermodynamic model, e-CPA ignores the effect of kinetic depolarization. The kinetic depolarization may explain 25-75% of the observed decrease in the relative static permittivity of solutions containing salts, but since this is a dynamic property, this kinetic depolarization shall not be included in thermodynamic modeling of electrolytes [152].

The dynamic contribution to the relative static permittivity has been a subject of debate since it was first discussed by Hubbard and Onsager [153] in 1977. The kinetic polarization may be described as a reduction, with respect to the pure solvent, in the relative static permittivity of the solution. Onsager and Hubbard published a theory which predicts a dielectric decrease due to a hydrodynamic effect [153-156]. This work is the most notable treatment for the kinetic polarization. The decrease is shown to be proportional to the product of the dielectric relaxation time of the solvent and the low frequency conductivity of the solution.
Figure 3.8 Predicted relative static permittivity of aqueous NaCl solution at 298.15 K and 101325 Pa by using the e-CPA EOS against experimental data [157-165].

On one hand, it has been argued that the kinetic depolarization is a dynamic property, and this effect should not be included in the thermodynamic modeling of electrolytes. On the other hand, the empirical models proposed for relative static permittivity applied in the context of thermodynamic models may introduce unphysical behavior [24]. Based on these considerations, we expect that the values calculated by e-CPA can be directly used for thermodynamic modeling of electrolytes.

When dissolved in solvents, positive and negative ions, temporarily bonded together by the electrostatic force of attraction, form distinct chemical species called ion-pairs [166]. Polydorou et al. provided direct evidence for such clustering by using combined neutron diffraction and reverse Monte Carlo study for aqueous Pr₄NBr [167]. Cavell and Knight explained that, when ions associate to form ion-pairs, an increase in the relative static
permittivity is anticipated in such solutions since the dipole moments of the ion-pairs are much larger than those of the solvent molecules [168]. Some measurements of relative static permittivity had been done for electrolyte solutions [122, 123, 169, 170], which give support for such an increase in the relative static permittivity. The hydrophobic effect causes the aggregation of hydrophobic groups in the presence of water or other polar solvents [126, 127]. The segregation of water and hydrophobic groups maximizes hydrogen bonding between molecules of water, and minimizes the area of contact between hydrophobic groups and water. Water may play an important role in the process of hydrophobic interactions, because the strength of hydrogen bonding in water is stronger than that of the van der Waals interaction. An interface will appear between the solute and water when hydrophobic effect occurs [126, 127]. Tetra-alkyl ammonium halides salt is a favorite class of model substances for the investigation of hydrophobic effect [171]. By using infrared spectroscopy, Stangret and Gampe [129] found that the average number of hydrogen bonds significantly increases in TBAX aqueous solution, and the hydrophobic effect might affect the thermodynamic properties of TBAX aqueous solutions. Unfortunately, the origin of the hydrophobic effect is not fully understood, and the basic molecular processes are not well understood, either.

It has been stated that ion-pairs [128] and hydrophobic interactions [128, 172] exist in aqueous QAS solutions even at moderate concentrations. In this manner, QAS can be treated as a ‘weak electrolyte’ [173]. Both ion-pairs and hydrophobic effects can cause water structure making [174], and strengthen the hydrogen bonding around ions, thus increasing the relative static permittivity. The relative static permittivity plays a very important role in thermodynamic modeling of electrolyte solutions when the primitive approach is employed. The predicted static permittivity from e-CPA is presented in Figure 3.9, in which calculation the polarizability of TBA$^+$ is $34.70 \times 10^{-40} \text{C} \cdot \text{m}^2 \cdot \text{V}^{-1}$, taken from Gilkerson and Stewart’s work [175]. The dot line represents an empirical equation
reported by Buchner et al. [128], in which there are no experimental data reported. It has been stated that ion-pairs [128] and hydrophobic interactions [128, 172] exist in TBAX aqueous solution even at moderate concentrations, in which manner, the TBAX could be treated as a ‘weak electrolyte’ [173].

Figure 3.9 Predicted relative static permittivity of the aqueous TBAB solution at 298.15 K using the e-CPA EOS against the empirical correlation from Buchner et al. [128] and experimental data from Kaatze [128, 176].

It can be seen from Figure 3.9 that the values of relative static permittivity from e-CPA decrease monotonically with increasing solute molality as is the case for other electrolyte solutions. Under low to medium concentrations, e-CPA gives reasonable relative static permittivity for thermodynamic modeling, as e-CPA ignores the effect of kinetic depolarization which should not be included in thermodynamic modeling.

On one hand, it needs to be pointed out that e-CPA does not take dissociation equilibrium into account for the fact that the
electrolytes are not fully dissociated [177], so the current version of e-CPA cannot describe the possible ion-pairs and hydrophobic effects. On the other hand, there are very few experimental data of the relative static permittivity published for aqueous TBAX solutions, so more systematic measurements are recommended.

### 3.3.2 Parameter Estimation Analysis

While some promising results were obtained with the e-CPA EOS, there have also been some challenges and uncertainties, both in the calculations, in the values of the model parameters and the available experimental data. It is meaningful to perform a more systematic study of the effect of different parameters in the e-CPA calculations.

In this part, we treat aqueous TBAB solution as the study object. In order to analyze the effect of ion radius, regression studies in the molality range up to 10 mol/kg water at 298.15 K are made, where the ion radius is fixed to a constant (the values of ion radius $r$ are set to 0.25 Å, 0.5 Å, 1.25 Å, 1.75 Å, 2.25 Å, 2.75 Å and 3.25 Å), and the Born radius $r_{\text{Born},i}$ is calculated from ion radius by using Eq. (3.3).

Table 3.10 presents the fixed and fitted parameters along with the RAD of mean ionic activity coefficients ($\gamma^m_\pm$), osmotic coefficients ($\Phi$) and liquid density ($\rho$). The results show that when fixing the radius of TBA$^+$, setting interaction parameter $\Delta U_{ij}^{\text{ref}}$ and CPA co-volume $b$ as adjustable parameters, a smaller fixed ion radius yields better results of mean ionic activity coefficients and osmotic coefficients, but worse results of liquid density.

The saturation pressure results using the parameters of Table 3.10 are very similar to the results presented in Figure 3.10.
Modeling of Aqueous Electrolyte Solutions

Table 3.10 Performance of e-CPA for TBAB aqueous solution (at 298.15 K) with different fixed ion size*.

<table>
<thead>
<tr>
<th>Fixed Values</th>
<th>Adjustable parameters</th>
<th>RAD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_i$ [Å]</td>
<td>$r_{Born,i}$ [Å]</td>
<td>$b$ [cm$^3$/mol]</td>
</tr>
<tr>
<td>0.25</td>
<td>1.10</td>
<td>91.4</td>
</tr>
<tr>
<td>0.50</td>
<td>1.35</td>
<td>93.8</td>
</tr>
<tr>
<td>0.75</td>
<td>1.60</td>
<td>97.4</td>
</tr>
<tr>
<td>1.25</td>
<td>2.10</td>
<td>104.7</td>
</tr>
<tr>
<td>1.75</td>
<td>2.60</td>
<td>111.2</td>
</tr>
<tr>
<td>2.25</td>
<td>3.10</td>
<td>116.3</td>
</tr>
<tr>
<td>2.75</td>
<td>3.60</td>
<td>121.5</td>
</tr>
<tr>
<td>3.25</td>
<td>4.10</td>
<td>125.5</td>
</tr>
</tbody>
</table>

* CPA co-volume and interaction parameter as adjustable parameters (the molality range in regression is 0.0912-10.0 mol/kg).

Figure 3.10 shows the relative static permittivity which is calculated.
from the new parameters (Table 3.10) when setting the interaction parameter $\Delta U_{ij}^{\text{ref}}$ and the CPA co-volume parameter $b$ as adjustable parameters. It can be seen that a smaller fixed ion radius can result in a larger value of relative static permittivity at a fixed salt concentration.

When setting the ion radius $r$, HV-NRTL energy parameter $\Delta U_{ij}^{\text{ref}}$ and Born radius $r_{\text{Born},i}$ as adjustable parameters, and the CPA co-volume parameter $b$ is calculated from ion radius by using Eq. (3.4), the modeling results are presented in Table 3.11 and Figure 3.11. From the predicted relative static permittivity in Figure 3.11, it can be concluded that if the ion radius, Born radius and CPA co-volume parameter become smaller, the relative static permittivity becomes unreasonably high, even though the results for mean ionic activity coefficients and osmotic coefficients become better.

Smaller ion radius means larger contribution to residual Helmholtz energy from the Debye–Hückel term. When the radius value of TBA$^+$ gets smaller, the results are better. It may be because the electrostatic interaction is mainly due to central small nitrogen ion, and alkyl chains give smaller contribution to the electrostatic interactions.

Table 3.11 Performance of e-CPA for aqueous TBAB solution with ion size $r$, Born radius $r_{\text{Born},i}$ and interaction parameter $\Delta U_{ij}^{\text{ref}}$ as adjustable parameters

<table>
<thead>
<tr>
<th>Adjustable parameters</th>
<th>$b$ [cm³/mol]</th>
<th>RAD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r$ [Å]</td>
<td>$r_{\text{Born},i}$ [Å]</td>
<td>$\Delta U_{ij}^{\text{ref}} / R$ [K]</td>
</tr>
<tr>
<td>0.835</td>
<td>0.59</td>
<td>-693.8</td>
</tr>
</tbody>
</table>

* The molality range in regression is 0.0912-10.0 mol/kg.
Ion-pairs and hydrophobic effects are important for organic salts. Therefore, it is worth trying to regress data at different salt concentrations, and then, compare the predictions at other concentrations not used in the parameter estimation. In this work, for the aqueous TBAB solution, the data with molality $\leq 1.4 \text{ mol/kg water}$, molality $\leq 10 \text{ mol/kg water}$, and molality $\leq 27 \text{ mol/kg water}$ are used for regression. In this regression, the HV-NRTL interaction parameter is set as the only adjustable parameter at 298.15 K, and the ion radius of TBA$^+$ is fixed to 2.25 Å, the Born radius is calculated from ion radius by using Eq. (3.3), and the CPA co-volume $b$ is calculated from ion radius by using Eq. (3.4). In order to validate the applicability of the regressed parameters, they are used to predict the mean ionic activity coefficients and osmotic coefficients for other molality ranges. The modeling results of the aqueous TBAB solution for this investigation are shown in Table 3.12 and Figure 3.12.

From the results of Table 3.12, it can be seen that when fixing the ion radius, the RAD for molality $\leq 1.4 \text{ mol/kg water}$ is smaller than at
the other molality ranges. When using the parameters from molality \( \leq 10 \text{ mol/kg water} \) to predict for other ranges, the results seem to be worse. The regressed parameters and results for molality \( \leq 1.4 \text{ mol/kg water} \) are similar with the results of molality \( \leq 27 \text{ mol/kg water} \). The results of molality \( \leq 10 \text{ mol/kg water} \) are worse, and the absolute value of HV-NRTL energy parameter gets the largest value.

Table 3.12 Performance of e-CPA for aqueous TBAB solution (at 298.15 K) with one adjustable parameter \( (\Delta U_{ij}^{ref}) \) from different experimental data.

<table>
<thead>
<tr>
<th>m range (Regression)</th>
<th>( r ) [Å]</th>
<th>( \Delta U_{ij}^{ref} / R ) [K]</th>
<th>RAD (%)</th>
<th>m range (Prediction)</th>
<th>( y_m^\pm )</th>
<th>( \Phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \leq 1.4 )</td>
<td></td>
<td>-95.3</td>
<td></td>
<td>( \leq 1.4 )</td>
<td>3.8</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \leq 10 )</td>
<td>10.6</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \leq 27 )</td>
<td>16.5</td>
<td>19.8</td>
</tr>
<tr>
<td>( \leq 10 )</td>
<td>Fix 2.25</td>
<td>-114.9</td>
<td></td>
<td>( \leq 1.4 )</td>
<td>10.0</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \leq 10 )</td>
<td>7.2</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \leq 27 )</td>
<td>22.4</td>
<td>18.2</td>
</tr>
<tr>
<td>( \leq 27 )</td>
<td></td>
<td>-101.0</td>
<td></td>
<td>( \leq 1.4 )</td>
<td>4.4</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \leq 10 )</td>
<td>9.7</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \leq 27 )</td>
<td>16.7</td>
<td>19.2</td>
</tr>
</tbody>
</table>
Figure 3.12 Predicted mean ionic activity coefficients and osmotic coefficients of aqueous TBAB solution at 298.15 K using the e-CPA EOS (with the parameters in Table 3.12) against experimental data [109, 110].

Additionally, in order to analyse the influence of the ion radius further, both ion radius $r$ and interaction energy parameter $\Delta U^r_{ij}/R$ are treated as adjustable parameters. Table 3.13 lists the results and parameters. For the molality $\leq$10 mol/kg case in Table 3.13, the parameters are the same as for the standard salt-specific parameters of Table 3.9. It can be seen that very small ion radius value can give very good results. From the above results, the difference of RAD among the three molality ranges is relatively large. From Table 3.13, the deviation of mean ionic activity coefficients and osmotic coefficients sharply becomes large at the molality range 1.5-10 mol/kg water.

When the Born radius and CPA co-volume parameter are estimated from ion radius, very small TBA$^+$ radius values can give excellent results of mean ion activity coefficients and osmotic coefficients. But small TBA$^+$ radius values are physically less
sound, also resulting in unreasonable relative static permittivity, thus small TBA$^+$ radius size values lead to small and unreasonable CPA co-volume parameters. The adjustable parameters which are fitted to 10 mol/kg water are reasonable.

Table 3.13 Performance of e-CPA for aqueous TBAB solution with two adjustable parameters (ion radius $r$ and interaction parameter $\Delta U_{ij}^{ref}$) from experimental data with different molality range $^\ast$.

<table>
<thead>
<tr>
<th>m range (Regression)</th>
<th>Adjustable parameters</th>
<th>Calculated from $r$</th>
<th>RAD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r$ [Å]</td>
<td>$\Delta U_{ij}^{ref}$/R [K]</td>
<td>$r_{Born,i}$ [Å]</td>
</tr>
<tr>
<td>≤1.4</td>
<td>0.33</td>
<td>-457.9</td>
<td>1.18</td>
</tr>
<tr>
<td>≤27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>≤10</td>
<td>2.25</td>
<td>-114.9</td>
<td>3.10</td>
</tr>
<tr>
<td>≤27</td>
<td>2.05</td>
<td>-123.9</td>
<td>2.90</td>
</tr>
<tr>
<td>≤27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>≤1.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>≤27</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^\ast$ The Born radius $r_{Born,i}$ of cation is calculated from ion radius by using Eq. (3.3), the Born radius of anion is calculated from ion radius by using Eq. (3.2), the CPA co-volume $b$ is calculated from ion radius by using Eq. (3.4).

This section performs a systematic study of the effect of different parameters in the e-CPA calculations, the results show that ion radius is the role parameter in calculation, and other parameters are also important.
3.3.3 Model Comparison

Thermodynamic modeling for aqueous QAS solutions has been investigated with different approaches in the literature. Table 3.14 summarizes the properties studied with different models for the aqueous QAS solutions in order to present a clear comparison of the different methodologies.

In terms of general modeling approach, SAFT-VRE, MPT, e-CPA and e-NRTL considered TBAX as strong electrolytes in water, and the ion-pairs are not considered. Only AMSA-NRTL [100] can treat micelle formation because AMSA-NRTL electrolyte model includes a term of ion-pairs contribution. No model takes the possible hydrophobic effect into account.

In terms of density performance, in the $\phi - \gamma$ approaches, the density of TBAX aqueous solutions was determined using correlation equations. In the $\phi - \phi$ approaches, both SAFT-VRE and e-CPA overestimate the experimental densities of TBAB solutions. Paricaud explained that it is because SAFT-VRE cannot represent formation of low-density ice-like structures around the large hydrophobic TBA$^+$ [21]. As reported above, the diameter of TBA$^+$ in all three models are smaller than the values published in literature. Moreover, as shown in Table 3.10, the bigger the diameter of TBA$^+$ is used, the better density is obtained. These imply that the models might have not captured the essential aspects of physics of TBAX aqueous solution. It is demonstrated in this work that with a Peneloux parameter e-CPA can give a very good agreement with experimental data.

In terms of electrostatic contributions, SAFT-VRE uses a MSA term in Paricaud’s work [21], MPT uses a Debye–Hückel term in Ma et al.’ work [98], and in this work, e-CPA combines Debye–Hückel and Born terms. Naturally it is the developer’s choice to use MSA or Debye–Hückel in an EOS model, as it has been proved that they perform similarly [178]. Different than both SAFT-VRE and MPT, e-CPA explicitly takes ion hydration into account via the Born equation, and the relative static permittivity of electrolyte solution is
calculated by a theoretical model, which extends the framework developed by Onsager, Kirkwood, and Fröhlich [146-148] to associating mixtures. This may increase the complexity of the model but make the model more reasonable.

In principle, SAFT-VRE, MPT, e-CPA and e-NRTL are ion specific by nature, while it is the users’ choice when a salt-specific or an ion-specific should be followed, as well as the number of adjustable parameters to be used.

In Paricaud’s work [21], the salt-specific approach was used in SAFT-VRE for TBAB, TBAC and TBAF aqueous solutions. For one single salt/single solvent system, there are three adjustable parameters at 298.15 K, one temperature dependent parameter. In the work of Ma et al. [98], the ion-specific approach was used in MPT for TBAB and TBAF aqueous solutions. For one single salt/single solvent system, there are four adjustable parameters at 298.15 K, no temperature dependent parameter.

The salt-specific approach was used in AMSA-NRTL for TBAB aqueous solution. For one single salt/single solvent system, AMSA-NRTL has five adjustable parameters. e-NRTL uses salt-specific approach, it has been applied for TBAB, TBAC and TBAF aqueous solutions. For one single salt/single solvent system, e-NRTL has two adjustable parameters. The temperature dependence of interaction energy parameters was neglected in AMSA-NRTL and e-NRTL for modelling of TBAX aqueous solution systems [101-104].

Unlike the approach using a different ion size for each salt in SAFT-VRE [21], in the presented e-CPA approach, the diameter of TBA$^+$ is first fitted to the TBAB data, and then the same value is used for other TBAX systems. In addition to the TBA$^+$ diameter, there are one adjustable interaction parameter at 298.15 K, and two temperature dependent interaction parameters.
Table 3.14 Properties studies for TBAX aqueous solutions at 298.15 K

<table>
<thead>
<tr>
<th>Approach Models</th>
<th>Max molality [mol/kg]</th>
<th>Adjustable parameters</th>
<th>Performance (RAD [%])</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\gamma_\infty / \phi$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TBAB</td>
<td>10.0</td>
<td>1.6</td>
<td>7.2/ 6.6%</td>
</tr>
<tr>
<td>TBAC</td>
<td>10.0</td>
<td></td>
<td>5.9% 4.5%</td>
</tr>
<tr>
<td>TBAF</td>
<td>1.6</td>
<td></td>
<td>4.8% 2.6%</td>
</tr>
<tr>
<td>TBAB</td>
<td></td>
<td>1 (TBA⁺ size, from TBAB) + 1 (interaction param)</td>
<td>9.2%(w/o $C_i$)</td>
</tr>
<tr>
<td>TBAC</td>
<td></td>
<td></td>
<td>0.2%(with $C_i$)</td>
</tr>
<tr>
<td>TBAF</td>
<td></td>
<td></td>
<td>7.7%(298.15 K)</td>
</tr>
<tr>
<td>$\phi - \gamma$</td>
<td></td>
<td></td>
<td>5.9%(323.15 K)</td>
</tr>
<tr>
<td>SAFT-VR E [21]</td>
<td>10.0</td>
<td>1.6</td>
<td>3.9/</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.6%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>EOS+NRT L+correlation on [105]</td>
<td>-</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>$\phi - \gamma$</td>
<td></td>
<td></td>
<td>3.29%</td>
</tr>
<tr>
<td>EOS+e-N RTL [101-103]</td>
<td>27.0</td>
<td>15.0</td>
<td>1.6</td>
</tr>
<tr>
<td>EOS+AM SA-NRTL [104]</td>
<td>21.0</td>
<td>-</td>
<td>5</td>
</tr>
</tbody>
</table>

* e-CPA with parameters in Table 3.9. For $\phi - \gamma$ approach, we treat the number of adjustable parameters in activity coefficient model as the total number of adjustable parameters. # It is composition and volume dependent.
3.4 Conclusion

This section presents a theoretical study on the thermodynamic modeling for aqueous solutions of QAS by using the e-CPA EOS, which includes Debye–Hückel and Born terms for electrostatic contributions. Several properties of these aqueous solutions as well as various modeling approaches have been considered in order to investigate the effect of the number and type of adjustable parameters used.

The thermodynamic modeling of QAS systems is challenging, among other reasons because the \( R_4N^+ \) ion has alkyl chains and low charges, thus exhibiting hydrophobic-like character. There is evidence that the unusual solution behavior of QAS is related to the hydrophobicity of these salts in aqueous solutions.

The e-CPA parameters (ionic size of \( R_4N^+ \), ion-water interaction parameters) are estimated from mean ionic activity coefficients and osmotic coefficients. Using the obtained parameters, e-CPA was subsequently used to predict the densities and relative static permittivity of aqueous TBAB solutions. It can be concluded that e-CPA can correlate satisfactorily the mean ionic activity coefficients and osmotic coefficients of aqueous QAS solutions over extensive temperature and concentration ranges. e-CPA with the parameters obtained in this work cannot describe the enhancement of the relative static permittivity due to the ion-pairs and hydrophobic effects. Adding dissociation equilibrium to the model is a potential solution for organic salt solutions where ion-pairs and hydrophobic effects exist.
Chapter 4. Modeling of Gas Solubility

This chapter presents gas solubility calculations in aqueous solutions of several quaternary ammonium salts and metal halide salts, as well as the discussion of salting effects.

The main parts of this chapter are based on these two published manuscripts:


Chapter structure and contents:
4.1 Gas Dissolution in Water
4.2 Aqueous Solutions of Inorganic Salts
4.3 Aqueous Solutions of Quaternary Ammonium Salts
4.1 Gas Dissolution in Water

4.1.1 Mechanism of Gas Dissolution

Before proposing the results, to better understanding the mechanism of gas dissolution, it would be necessary to review some theories. The definition of gas solubility is the maximum quantity of gas that can dissolve in a certain quantity of solvent or quantity of solution at a specified temperature or pressure (in the case of gaseous solutes) [179]. Fu et al. [180] proposed two mechanisms of gas dissolution in water: interstitial filling and hydration. By interstitial filling is means that gas molecules diffusion fills the interstices between liquid water molecules, and both temperature and pressure have substantial effects on the interstitial filling. Hydration is the combination and decomposition process of gas and water molecules, and it is a reversible process. Eley [181] stated that the greater the number of cavities existing in water, the higher is the gas solubility. Temperature, pressure and salt concentration play important roles in determining the gas solubility. Gas solubility decreases as temperature increases, the physical explanation is that when most gases dissolve in solution, the process is exothermic, and heat is released as the gas dissolves. Temperature increase causes an increase in kinetic energy. The higher kinetic energy causes more motion in the gas molecules which break intermolecular bonds and escape from solution [182, 183]. This phenomenon is very similar to that vapor pressure increases with temperature. The dissolution of gases in water is an equilibrium process, and when the pressure increases, the gas molecules are forced into the solution since this will best relieve the pressure that has been applied [182, 183].

Water is a poor solvent for non-polar solutes [184]. CO₂, N₂, CH₄, C₂H₆ are not very soluble in water, the dissolution of CO₂ in water contains an additional two acid equilibrium, which can increase the solubility of CO₂ in water [185].
4.1.2 Solubility of Gas in Pure Water

Before modelling the electrolyte systems, the performance of model for H$_2$O+gas binary systems should be studied. The e-CPA can reduce to CPA in the absence of electrolytes. Table 4.1 list the pure component model parameters of gases.

Table 4.1 CPA parameters of pure component.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_c$ [K]</th>
<th>$b$ [L/mol]</th>
<th>$\Gamma$ [K]</th>
<th>$c_1$</th>
<th>Association scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ [186]</td>
<td>304.21</td>
<td>0.0272</td>
<td>1551.222</td>
<td>0.7602</td>
<td>n.a.</td>
</tr>
<tr>
<td>N$_2$ [187]</td>
<td>126.20</td>
<td>0.02605</td>
<td>634.070</td>
<td>0.49855</td>
<td>n.a.</td>
</tr>
<tr>
<td>CH$_4$ [186]</td>
<td>190.56</td>
<td>0.02910</td>
<td>959.028</td>
<td>0.44718</td>
<td>n.a.</td>
</tr>
<tr>
<td>C$_2$H$_6$ [186]</td>
<td>305.32</td>
<td>0.04290</td>
<td>1544.548</td>
<td>0.58463</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

In Table 4.1, ‘n.a.’ respects Non-association, $T_c$ is critical Temperature, $b$ is CPA co-volume parameter, $\Gamma$ is CPA reduced energy parameter, $c_1$ is CPA alpha-function T-dependence (Eq. (2.25) of Chapter 2).

The evaluation results are presented in Table 4.2 together with temperature-dependent binary interaction parameters, and CO$_2$ is not considered as a self-associating fluid in this work. It needs to be pointed out that the existence of two liquid phases of H$_2$O+CO$_2$ has not been taken into account in this work, and the same strategy is applied for the modelling of H$_2$O+salt(s)+CO$_2$ systems below, mainly due to lack of experimental data for the two liquid phases. On one hand, it can be seen that e-CPA can reasonably correlate the solubility of CO$_2$, N$_2$ in water with the binary interaction parameter from literature, and large deviations are only found at low pressure and high temperature. On the other hand, with the published interaction parameters [188], e-CPA cannot describe the CH$_4$ solubility accurately for the experimental data collected in this work. This might be because the temperature range and data used in correlation are different, and it leads to a new correlation as given in Table 4.2.
Table 4.2 Modelling performance of gas solubility in pure H₂O.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$k_{ij}$</th>
<th>T range [K]</th>
<th>Evaluation results</th>
<th></th>
<th></th>
<th>Np</th>
<th>RAD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>T range [K]</td>
<td>P [MPa]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>-0.15508+0.000877T</td>
<td>298.15-477.6</td>
<td>273.75-473.15</td>
<td>0.095-82.88</td>
<td>328</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>0.6769-213.5/T [188]</td>
<td>274.0-473.0</td>
<td>274.19-444.26</td>
<td>0.101-100.0</td>
<td>206</td>
<td>12.2</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>0.8243-245.33/T</td>
<td>274.19-444.26</td>
<td>274.19-444.26</td>
<td>0.101-100.0</td>
<td>206</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>1.0741 – 368.3066/T [189]</td>
<td>273 - 366</td>
<td>274.1-628.0</td>
<td>0.534-101.325</td>
<td>176</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.6091-166.253/T</td>
<td>-</td>
<td>274.26-444.26</td>
<td>0.101325-68.94</td>
<td>308</td>
<td>9.5</td>
<td></td>
</tr>
</tbody>
</table>

a. verification work; b. interaction between water and gas; c. RAD is the relative average deviation [%] of mole fraction of gas in liquid phase; d. Np is number of data points; * The first T-range [K] is the temperature used in the binary interaction parameter correlations. Np is number of data points, H₂O-CO₂ data source: [190-200] and H₂O-CH₄ data source: [201-207]; C₂H₆+H₂O data source: [205, 206, 208-215]; N₂+H₂O data source: [216-220].

4.1.3 Salting Effects

Salting-in and salting-out are defined as the increment and reduction of the solubility of a gas due to the presence of ionic species in a solvent [221].

The salting-out effect of some salts (such as NaCl) on gas is mainly from the ions solvation, which makes the dissolved gas molecules out of the interstice of water molecules [184]. Carvalho et al. [222] and Wiebe and Gaddy [194] gave some description for gas solubility in NaCl aqueous solution: The increase in the brine’s salinity leads to a reduction of CO₂ dissolution, regardless of its pressure and temperature. The decreased CO₂ solubility in a brine solution can be explained by ‘solvation’: involvement of water molecules in ions solvation make the dissolved CO₂ out of the water interstices, and the pressure dependency of the solubility reduces as the pressure increases. At low salinities, the effect was not that pronounced.
However, some salt ions, such as quaternary ammonium cations (R₄N⁺), cause instead of the salting-in of hydrophobic solutes [184, 223]. It is believed that R₄N⁺ ions that have alkyl chains and low charges exhibit hydrophobic character, the change of water structure brought about by the presence of R₄N⁺ is an important factor responsible for the salting-in process [224, 225].

4.2 Aqueous Solutions of Inorganic Salts

Thermodynamic modeling is an attractive approach for calculating gas solubilities. Extensive thermodynamic modeling studies have been made for calculating the solubilities of CO₂ and CH₄ in aqueous solutions of inorganic salts. The so-called φ-γ approach has played a vital role in these studies [190, 191, 226-242]. The equations of state (EOS) of Peng-Robinson (PR) [243], SRK [45], Redlich-Kwong (RK) [244], Virial truncated after the second term [234, 236], Patel and Teja (PT) [245] and Perturbed-Chain statistical associating fluid theory (PC-SAFT) [246, 247] have been used for modeling the fugacity coefficient (φ), while LIFAC [248], extended UNIQUAC [249], NRTL activity coefficient model [250], Pitzer’s equation [57], electrolyte NRTL [15, 251] and empirical correlations [190] are typical choices for the activity coefficient (γ). This approach usually requires many adjustable parameters (even up to 20 for a single salt solution [241]), and the application of this approach in multi-salt solutions has not been seen.

An electrolyte EOS for both vapor and liquid phases provide a more consistent framework, as well as the possibility to calculate other properties, e.g. density and surface tension. Some practices have also been done for modeling the solubility of CO₂ and CH₄ in aqueous salt solutions [17-20, 22, 23, 252-257]. Unfortunately, on one hand, a few electrolyte EOS can predict gas solubility over a wide range of conditions with accuracy close to the experiment accuracy, and fewer studies made systematic investigations. On the other hand, if the electrolyte EOS is set up for ions, it shall in principle be working for multi-salt solutions. To the best of our
knowledge, however, no research on modeling gas solubility in aqueous multi-salt solutions has been reported for electrolyte EOS, and the most studied system is H₂O+NaCl+CO₂.

### 4.2.1 Data analysis

Sometimes experimental data may represent large uncertainties because of the experimental apparatus, measurement methods and/or operations. In order to obtain accurate binary interaction parameters between ion and gas, and ensure that the model describes the actual phase behavior, experimental data have been analyzed and filtered prior to modeling.

Duan and Sun [235] collected and analysed the solubility data of CO₂ in aqueous NaCl solution, and concluded that most experimental data sets are consistent within errors of about 7%. Yan et al. [192] made an extensive review for the solubility data of CO₂ in aqueous NaCl solution, and concluded that the solubility data measured by Kiepe et al. [191] and Drummond [258] are doubtful. Yan et al. [192] pointed out further that most high-pressure solubility data of CO₂ in aqueous NaCl solution are from three data sources: Takenouchi and Kennedy [259], Rumpf et al. [234], and Koschel et al. [260]. Duan et al. [9] reviewed experimental data of the CH₄ solubility in aqueous CaCl₂ solution from Blanco and Smith [261], and determined the valid range, i.e. from 25 to 125 °C and from 100 to 600 bar. Duan et al. [9] pointed out that the most comprehensive data reported for the CH₄ solubility in aqueous NaCl solution are from Blount et al. [262], while Price et al. [263] pointed out an experimental error in Blount et al.’s work [262], and concluded that about 70% of the data points for pressure below 300 bar have a high deviation (10-35%). Duan et al. [9] pointed out that the data from Duffy et al. [264] and Michels et al. [265] showed large uncertainties. Moreover, Duan et al. [9] suggested not using the solubility data of CH₄ in aqueous NaCl solution from Barta and Bradley [266] and Drummond [258]. In a later work, Duan et al. [267] pointed out that experimental data
for CH₄ in aqueous CaCl₂ solution from Duffy et al. [264] and Michels et al. [265] are unreliable, as are those in NaCl solutions, due to adopting an inaccurate pressure decline technique. Pérez-Salado et al. [239] stated that the data from Kiepe et al. [191] have low credibility. It is known from Takenouchi and Kennedy [193] and Tödheide and Franck [268] that the change of the solubility of CO₂ with pressure at temperatures above 538 K differs sharply from that at temperatures below 538 K. In this work, therefore, we set the modelling temperature lower than 538 K. Moreover, the range of salt molality of most collected data follows the work of Maribo-Mogensen et al [24], i.e. NaCl: 6 mol/kg water, KCl: 6 mol/kg water, CaCl₂: 3 mol/kg water, MgCl₂: 2 mol/kg water, and Na₂SO₄: 2 mol/kg water.

The solubility data of CO₂ in aqueous solutions of salts other than NaCl and CaCl₂, and the solubility data of CH₄ in aqueous solutions of salts other than NaCl, KCl and CaCl₂ are limited. Moreover, the overlapping space is very small, and a clear conclusion about the reliability of these various sources cannot be reached. For the gas solubility in aqueous multi-salt solutions, the experimental data are limited and scattered. Therefore, we consider all these collected data of aqueous multi-salt solutions reliable.

4.2.2 Modeling Results

Gas solubility in electrolyte solution is calculated by a two-phase PT-flash with the successive substitution method [269, 270]. It is assumed that there is no salt in vapor phase. The parametrization is the same as that in Chapter 3.

4.2.2.1 Single-salt Systems

Table 4.3 summarizes the ion-gas interaction parameters and the performance of e-CPA on correlating the gas solubility with Approach A. It can be seen, on one hand, that the energy interaction parameters $\Delta U_{ij}^{ref} / R$ of ion-CO₂ and ion-CH₄ follow the
same order: NaCl>KCl>CaCl₂>MgCl₂, and $\Delta U_{ij}^{ref}/R$ of ion(Na₂SO₄)-CO₂ has the highest value: 1449.66 K. On the other hand, the deviations are very satisfactory, less than the aforementioned experimental uncertainty 7% for most of the investigated systems. For the results of H₂O-NaCl-CH₄ system, the larger deviations of the solubility of CH₄ [262] might be from high temperatures (up to 513.15 K), as the binary interaction parameters between CH₄ and H₂O are obtained by fitting the data up to 444.26 K, in a combination of the doubtful data [262] as discussed above.

Table 4.3 lists the details of the modelling results for all three approaches. Approach A shows an overall better performance than Approaches B and C, which is to be expected as there are more adjustable parameters. It needs to be pointed out that Approach A, from a mathematical point of view, is in general more sensitive to the data used in the parameter fitting than the two other approaches. Approaches A and B can be recommended when there are enough data over a wide range of temperature available, while Approach C is recommended if limited data are available and extrapolations are required. With Approach C, the binary interaction parameters of Na⁺/Cl⁻-CO₂ and that of Na⁺/Cl⁻-CH₄ are not the same but close to what were reported by Maribo-Mogensen et al. [24] ($\Delta U_{ij}^{ref}/R = 816.4$K versus 724.8 K for Na+/Cl--CO₂, and $\Delta U_{ij}^{ref}/R = 1329$ K versus 1128 K for Na+/Cl--CH₄). The small differences are due to the different binary interaction parameters between H₂O and gas, as well as the different experimental data. It is a good indication that Approach C is not so sensitive to the data, and with this approach Maribo-Mogensen et al. [24] showed the predictive capability of e-CPA for the solubility of CO₂ and CH₄ in NaCl containing systems. In the following part, Approach A is used except for the H₂O+MgCl₂+CH₄ system which is modeled with Approach C because of the limited number of data points.
Figure 4.1 Comparison of the modeling results against the experimental data of the solubility of (a) CO$_2$ in aqueous NaCl solution at 323.15 K [192, 260, 271]; (b) CH$_4$ in aqueous NaCl solution at 298.15 K [272].
Table 4.3 Modelling performance for gas solubility in aqueous single salt solution.

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a. Np is number of data points.
Figure 4.2 Comparison of the modeling results against the experimental solubility of CH$_4$ in aqueous NaCl solutions at 324.65 K [219].

Figure 4.1 presents the solubilities of CO$_2$ and CH$_4$ in aqueous NaCl solution as a function of pressure at different salinity and a constant temperature. Figure 4.1 (a) shows that the solubility of CO$_2$ decreases as the NaCl concentration increases, which is a typical ‘salting-out’ affect, defined as the reduction of the solubility of a gas due to the presence of ionic species in a solvent [286]. Carvalho et al. [222] and Wiebe et al. [194] found that the increase of the brine’s salinity leads to a reduction of CO$_2$ dissolution, regardless of the system pressure and temperature. They explained the reduction of the solubility of CO$_2$ in a brine solution on ‘solvation’ terms: involvement of H$_2$O molecules in ions solvation makes the dissolved CO$_2$ out of the interstice of water molecules. They also pointed out that the salting-out effect was not that pronounced at low salinities, and the pressure dependency of the solubility reduces as the pressure increases [194, 222].

Similar with CO$_2$, it can be seen from Figure 4.1 (b) that e-CPA can correlate very well the solubility of CH$_4$ in aqueous NaCl solution, and the solubility of CH$_4$ decreases as the NaCl concentration increases.
Combining with Figure 4.2, which presents the solubility of CH₄ in aqueous NaCl solution at different salinity and temperatures, it is also observed that the solubility of CH₄ decreases as temperature increases and pressure decreases, which is consistent with the literature [219, 272].
Modeling of Gas Solubility

Figure 4.3 shows the calculated gas solubility in aqueous KCl solution as a function of pressure at different salinity and temperatures. It can be seen, similar to the aqueous NaCl solution, that gas solubility in aqueous KCl solution decreases as temperature increases and as pressure decreases. As the molality of KCl increases, the gas solubility decreases significantly, which means that KCl has a salting-out effect on the gas solubilities of CO$_2$ and CH$_4$ in H$_2$O.
Figure 4.4 Comparison of the modelling results against the experimental data of the solubility of (a) CO\textsubscript{2} in aqueous CaCl\textsubscript{2} solution at 349.15 K and 374.15 K [285]; (b) CH\textsubscript{4} in aqueous CaCl\textsubscript{2} solution at 298.15 K[261, 272].
Figure 4.5 Comparison of the modeling results against the experimental (a). CO$_2$ solubility in aqueous CaCl$_2$ solutions at 323.15 K [284]; (b). CH$_4$ solubility in aqueous CaCl$_2$ solutions at 298.15 K and 324.65 K [261].
Figure 4.6 Comparison of the modelling results against the experimental gas solubility in aqueous MgCl$_2$ solution: (a) CO$_2$ at 15 MPa[281]; (b) CH$_4$ at 298.15 K [272].
Figure 4.7 Comparison of the modelling results against the experimental solubility of CO$_2$ [236] in aqueous Na$_2$SO$_4$ solution.

Figures 4.4 (a) and (b) present the modeling results of the solubilities of CO$_2$ and CH$_4$ in the aqueous CaCl$_2$ solution, respectively. More modeling results of this system are presented in the Figure 4.5. It can be seen that CaCl$_2$ also has a significant salting-out effect on the solubilities of CO$_2$ and CH$_4$ in H$_2$O. The solubilities of both gases again increase as pressure increases. It is surprising that e-CPA can accurately capture the intersection of the solubility of CO$_2$ in aqueous CaCl$_2$ solution at 349.15K and 374.15K. This indicates that the temperature dependence of the salt-outing effect will depend on the pressure, which can also be deduced from Figure 4.4 (a). The solubility of CH$_4$ in aqueous CaCl$_2$ solution decreases as temperature increases.

Figures 4.6 (a) and (b) show the comparison of the modeling results and experimental data of the solubilities of CO$_2$ and CH$_4$ in aqueous MgCl$_2$ solution. Figure 4.6 (a) clearly shows that the solubility of CO$_2$ decreases as temperature increases at a constant
pressure and salinity, and the solubility of CH$_4$ increases as pressure increases. A significant salting-out effect is also observed. It can be seen that e-CPA can accurately correlate the solubilities of CO$_2$ and CH$_4$ in aqueous MgCl$_2$ solution. It is worth pointing out that the molality of CaCl$_2$ and MgCl$_2$ is smaller than that of NaCl and KCl, and a more detailed comparison is given below.

It can be seen from Figure 4.7 that e-CPA can reasonably correlate the solubility of CO$_2$ in aqueous Na$_2$SO$_4$ solution, and a similar behavior of the intersection of different temperatures occurring at higher pressures might be suspected, as seen from Figure 4.4 (a).

![Figure 4.8 Comparison of the modeling results against the experimental N$_2$ solubility in pure water [219, 287] and aqueous NaCl solution [219].](image-url)
Figure 4.9 Comparison of the modeling results against the experimental \( \text{C}_2\text{H}_6 \) solubility in aqueous solutions of NaCl [278, 288] and CaCl\(_2\) [278].

From Figures 4.8 and 4.9, it can be seen that e-CPA can correlate well the solubility of \( \text{N}_2 \) and \( \text{C}_2\text{H}_6 \) in aqueous NaCl solution and the solubility of \( \text{C}_2\text{H}_6 \) in aqueous CaCl\(_2\) solution. Figure 4.8 shows that with increasing NaCl molality, the \( \text{N}_2 \) solubility decreases significantly. This means that NaCl has a significant salting-out effect on \( \text{N}_2 \) solubility in water, and the salting-out effect becomes more significant at high pressure. Figure 4.9 shows that the solubility of \( \text{C}_2\text{H}_6 \) decreases as the NaCl and CaCl\(_2\) concentration increases. NaCl shows apparent ‘salting-out’ effect on \( \text{N}_2 \) and \( \text{C}_2\text{H}_6 \), and CaCl\(_2\) shows apparent ‘salting-out’ effect on \( \text{C}_2\text{H}_6 \).

**4.2.2.2 Multi-Salt Systems**

As discussed in Chapter 3 that the model with ion-molecular interaction parameters of single-salt can be used for aqueous multi-salt solutions. The predictions of the solubility of \( \text{CO}_2 \) in aqueous multi-salt solutions are presented in Tables 4.5-4.6 and
Figures 4.10-4.12. There are only few scatter data [289] of the solubility CH$_4$ in aqueous multi-salt solutions, Table 4.4 lists the results of these scatter data (RAD=5.9%). It can be seen from Tables 4.4-4.5 and Figures 4.10-4.12 that e-CPA can very reasonably predict the gas solubility in aqueous solutions over a wide range of salt mixtures. It needs to be pointed out that Liu et al.[273] did not clearly state which scale they used to report the solubility data, which are assumed to be salt-free in our modeling.

Table 4.4 Modelling performance of e-CPA for the solubility of CO$_2$ in aqueous multi-salt solutions with the binary interaction parameters from Table 4.3.

<table>
<thead>
<tr>
<th>Salts</th>
<th>T [K]</th>
<th>P [MPa]</th>
<th>I</th>
<th>Np</th>
<th>RAD b [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl+KCl</td>
<td>308.9-424.67</td>
<td>1.07-17.16</td>
<td>1.053, 1.69</td>
<td>22 [273, 283]</td>
<td>4.8</td>
</tr>
<tr>
<td>NaCl+CaCl$_2$</td>
<td>318.15</td>
<td>2.46-16.02</td>
<td>2.45</td>
<td>8 [273]</td>
<td>4.0</td>
</tr>
<tr>
<td>KCl+CaCl$_2$</td>
<td>318.15</td>
<td>2.09-15.87</td>
<td>2.25</td>
<td>8 [273]</td>
<td>5.0</td>
</tr>
<tr>
<td>NaCl+KCl+CaCl$_2$</td>
<td>308.15-328.15</td>
<td>1.34-15.85</td>
<td>1.00-3.20</td>
<td>75 [273]</td>
<td>6.1</td>
</tr>
<tr>
<td>NaCl+KCl+CaCl$_2$+MgCl$_2$</td>
<td>297</td>
<td>0.52-14.12</td>
<td>1.70, 2.65</td>
<td>84 [290]</td>
<td>15.7</td>
</tr>
</tbody>
</table>

In Table 4.4, Np is number of data points; a. ionic strength [mol/kg water]; b. for molality of gas solubility.

Table 4.5 Modelling performance of e-CPA of CH$_4$ solubility in aqueous multi-salt solutions at 298.15 K and 3.792 MPa, with ion-gas interaction parameters in Table 4.3 (Approach A).

<table>
<thead>
<tr>
<th>Molality of ions [mol/kg water]</th>
<th>m$_{\text{CH}_4}$ [mol/kg water]</th>
<th>exp$^a$ [289]</th>
<th>cal$^a$</th>
<th>RAD [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>m$_{\text{NaCl}}$</td>
<td>m$_{\text{KCl}}$</td>
<td>m$_{\text{MgCl}_2}$</td>
<td>m$_{\text{CaCl}_2}$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

exp and cal are the experimental and calculated CH$_4$ molality respectively.
Figure 4.10 Comparison of the modelling results against the experimental solubility of CO₂ [273] in aqueous solutions of two salts at T=318.15 K. The weight percentage of the two salts are given in the Figure.

Figure 4.11 Comparison of the modelling results against the experimental solubility of CO₂ [283] in the aqueous solutions of three salts at T=308.15 K. Weight ratio of NaCl, KCl and CaCl₂ is 1:1:1.
Figure 4.12 Comparison of the modelling results against the experimental CO₂ solubility [290] in two aqueous salt solutions: Brines A (mNaCl=1.001 mol/kg water, mKCl=0.101 mol/kg water, mCaCl₂=0.100 mol/kg water, mMgCl₂=0.100 mol/kg water), Brines B (mNaCl=1.396 mol/kg water, mKCl=0.047 mol/kg water, mCaCl₂=0.339 mol/kg water, mMgCl₂=0.061 mol/kg water) at 297 K.

In Figure 4.12, there is a discontinuous inflection point of gas solubility for each system, this may because that there exist two liquid phases for H₂O+CO₂ near the critical temperature.

4.2.3 Discussion

4.2.3.1 Salting-out Effects of Different Salts

It is known that different salts have different salting-out effects, and the ion concentration and ion charge are believed the two main factors. The studies of the ion hydration and ion-H₂O molecule interactions [291, 292] demonstrated that ions with smaller size
and higher charge bind H₂O molecules stronger, which weakens the capacity of helping solvent trap dissolved gas molecules. Anions usually have larger ionic radii than cations, so the hydration of cations is usually much stronger than that of anions [293]. In order to analyze the salting-out effect of different salts in detail, the solubility of CO₂ and CH₄ in different aqueous salt solutions are compared in Figures 4.13 and 4.14.

It can be seen from Figure 4.13 (a) that different salts exhibit different salting-out effects, and the salting-out effects on CO₂ follow a sequence of KCl<NaCl<CaCl₂≈MgCl₂<Na₂SO₄ with the same molality. This is consistent with the findings from Jacob and Saylor [290]. Na₂SO₄ shows the strongest salting-out effect on the solubility of CO₂ mainly because 1 mol Na₂SO₄ has 2 mol Na⁺. For KCl, NaCl, CaCl₂ and MgCl₂, the salting-out effect is significantly greater with divalent cations, because the ion charge is more important than ion size in relation to the salting-out effect in these aqueous solutions with the same salt molality.

KCl shows the weakest salting-out effect, mainly because K⁺ has a low charge density and it binds H₂O weakly, and there are more intervals to accommodate gas molecules [273, 281, 291, 292]. The low charge density of K⁺ comes from that K⁺, with charge of ‘+1’, has a relatively bigger size than Na⁺, Mg²⁺ and Ca²⁺ (Pauling Radius: K⁺-1.33 Å; Na⁺-0.95 Å; Ca²⁺-0.99 Å; Mg²⁺-0.65 Å). Kiepe et al. [191] observed that the salting-out effect of KCl is smaller than that of NaCl on the solubility of CO₂.
Modeling of Gas Solubility

Figure 4.13 Comparison of the solubility of CO$_2$ in aqueous solutions of different salts at 323.15 K [192, 260, 281, 284].

(a) different salts with same molality (1.0 mol/kg water)

(b) different salts with same ionic strength (1.0 mol/kg water)
Figure 4.13 (b) shows that the salting-out effects on CO₂ follow a sequence of KCl<CaCl₂<MgCl₂<NaCl with the same ionic strength, and this is consistent with the work of Zhao et al. [281]. It can also be observed from both Figures 4.13 (a) and (b) that MgCl₂ and CaCl₂ have similar salting-out effects. Portier et al. [227] pointed out that the salting-out effect on the solubility of CO₂ in aqueous CaCl₂ or MgCl₂ solutions is lower than that in aqueous NaCl solution of equivalent ionic strength, because Ca²⁺ and Mg²⁺ tend to form ion pairs easily with the anions present in solution at the equivalent ionic strength with NaCl. Figure 4.14 shows that the salting-out effects on the solubility of CH₄ follow a sequence of KCl<NaCl<MgCl₂≈CaCl₂ with the same molality, and MgCl₂ and CaCl₂ have similar salting-out effects.

![Figure 4.14 Comparison of the solubility of CH₄ in different electrolyte aqueous solutions with the same molality (1.0 mol/kg water) at 298.15 K and P=2.41 MPa [272].](image-url)
4.2.3.2 Model Comparison

Table 4.6 shows a comparison of different electrolyte EOS for gas solubility calculations in aqueous solutions of inorganic salts. In these electrolyte EOS, Zuo and Guo [19], Sun and Dubessy [22], Tan et al. [253], and Ji et. al. [23] assumed that the dielectric constant of electrolyte solution is equal to that of the solvent. Other models [17, 18, 20, 252, 254, 256, 257] take the effect of salt presence on dielectric constant into account. e-CPA uses a theoretical model for dielectric constant calculation, which eliminates the kinetic depolarization. Søreide and Whitson [20], Aasberg-Petersen et al. [18], Haghighi et al. [252], and Sun and Dubessy [22, 255] did not explicitly take the ion solvation contribution into account, while other models included the ion solvation contribution via the Born term, which is believed important for salting-out effects and thermodynamic modeling of other properties and behavior. Temperature dependency of ion-gas interactions is used in some works, and the most studied system is H$_2$O-NaCl-CO$_2$. Both Harvey and Prausnitz [17] and Rozmus et al. [256] stated that their models can be applied to multi-salt solutions flexibly. To be best of our knowledge, however, no electrolyte EOS has been really applied for calculating the gas solubility in aqueous multi-salt solutions. In this work, e-CPA has been extended to multi-salt systems without new adjustable parameters. Most of the electrolyte EOS listed in Table 4.6 perform satisfactorily at low salt molality. Harvey and Prausnitz model [17] overestimates CO$_2$ solubility (about 10-20%) at high salt molality. The model (ALS+DH) proposed by Aasberg-Petersen et al. [18] slightly overpredicts gas solubility at high salt molality, and the deviation between calculated and experimental values may in certain cases be 10-15%, while the deviations are somewhat larger for the aqueous CaCl$_2$ solution. The MPT EOS [19] shows inaccurate results for the CO$_2$ solubility in aqueous NaCl solution, and it can only applied over narrow temperature ranges, probably because the temperature-dependent parameters have not been used.
Although the Søreide-Whitson model \([20]\) is relatively simple, it uses two different sets of interaction parameters. Thus, it is essentially an inconsistent thermodynamic model, and it cannot reasonably describe the solubility of CO\(_2\) in aqueous solutions with high salt molality (by more than 20% at 50 °C in NaCl solution with molality=2 mol/kg water, and at pressures=100 bar). Tan et al.’s model \([253]\) (CPA+PMSA) performs poorly at high molality and pressure. Courtial et al. \([254]\) used some unreliable experimental data for modelling, and the deviations of solubility are large. Sun and Dubessy \([22, 255]\) applied their model (SAFT-LJ+MSA) to calculate the solubility of CO\(_2\) in aqueous NaCl solution (range from 273 to 573 K, from 0 to 1000 bar, and from 0 to 6 mol/kg NaCl). The deviation for the solubility of CO\(_2\) with NaCl molality lower than 4 mol/kg is 3%. Schreckenberg et al. \([257]\) stated that the performance of their model for calculating the solubility of CO\(_2\) is not good at high salt molality.

### Table 4.6 Summary of modelling of gas solubility with electrolyte EOS.

<table>
<thead>
<tr>
<th>Ref</th>
<th>EOS</th>
<th>Elect. Terms</th>
<th>Ion-Gas IPs</th>
<th>Salts</th>
</tr>
</thead>
<tbody>
<tr>
<td>[20]</td>
<td>PR</td>
<td>None</td>
<td>N(_2): 4 (T-dep (^a))</td>
<td>NaCl</td>
</tr>
<tr>
<td>[20]</td>
<td>PR</td>
<td>None</td>
<td>CO(_2): 6 (T-dep)</td>
<td></td>
</tr>
<tr>
<td>[20]</td>
<td>PR</td>
<td>None</td>
<td>H(_2)S: 2 (T-dep)</td>
<td></td>
</tr>
<tr>
<td>[17]</td>
<td>P-LJ (^b)</td>
<td>MSA+Born</td>
<td>1 (T-ind (^c))</td>
<td>NaCl, CaCl(_2)</td>
</tr>
<tr>
<td>[18]</td>
<td>ALS</td>
<td>DH</td>
<td>1 (T-ind)</td>
<td>NaCl, CaCl(_2)</td>
</tr>
<tr>
<td>[19]</td>
<td>PT</td>
<td>DH</td>
<td>1 (T-ind)</td>
<td>NaCl, CaCl(_2)</td>
</tr>
<tr>
<td>[24] (^d)</td>
<td>CPA</td>
<td>DH+Born</td>
<td>3 (T-dep)</td>
<td>NaCl, CaCl(_2), KCl, MgCl(_2), Na(_2)SO(_4), as well as multi-salt</td>
</tr>
<tr>
<td>[252]</td>
<td>CPA</td>
<td>DH</td>
<td>5 (T-dep)</td>
<td>NaCl, CaCl(_2), KCl, MgCl(_2)</td>
</tr>
<tr>
<td>[253]</td>
<td>CPA</td>
<td>PMSA+Born</td>
<td>3 (T-dep)</td>
<td>NaCl</td>
</tr>
<tr>
<td>[254]</td>
<td>CPA</td>
<td>MSA+Born</td>
<td>3 (T-dep)</td>
<td>NaCl</td>
</tr>
<tr>
<td>[253]</td>
<td>PC-SAFT</td>
<td>PMSA</td>
<td>3 (T-dep)</td>
<td>NaCl</td>
</tr>
<tr>
<td>[22]</td>
<td>SAFT-LJ</td>
<td>MSA</td>
<td>3 (T-dep)</td>
<td>NaCl</td>
</tr>
<tr>
<td>[256]</td>
<td>PPC-SAFT</td>
<td>MSA+Born</td>
<td>Neglected</td>
<td>NaCl</td>
</tr>
<tr>
<td>[257]</td>
<td>SAFT-VR</td>
<td>MSA+Born</td>
<td>3 (T-dep)</td>
<td>NaCl</td>
</tr>
<tr>
<td>[23]</td>
<td>SAFT1</td>
<td>RPM</td>
<td>1 (T-ind)</td>
<td>NaCl</td>
</tr>
</tbody>
</table>
 Modeling of Gas Solubility

- T-dep: Temperature-dependent;
- Short-range perturbed term with Lennard-Jones potential;
- T-ind: Temperature-independent;
- This work; IPs is interaction parameter(s).

4.2.4 Conclusion

The solubilities of CO₂ and CH₄ in several aqueous solutions of inorganic salts have been studied systematically with the e-CPA EOS. In this section. It can be concluded that e-CPA gives accurate agreements with experimental data of H₂O-gas and H₂O-salt binary systems. With temperature-dependent ion-gas interaction parameters, e-CPA also gives excellent agreement with experimental gas solubility data over wide ranges of temperature, pressure and salt molality. e-CPA also predicts reasonable agreements with experimental gas solubility data in aqueous multi-salt solutions, without new adjustable parameters. Moreover, e-CPA shows a good performance on the salting-out effects from temperature and pressure as well as from ion size, charge density and salt concentration.

4.3 Aqueous Solutions of Quaternary Ammonium Salts

Relatively few thermodynamic modeling studies of gas solubility have been proposed so far for QAS systems. Paricaud [21] used SAFT-VRE to describe the fluid phase. In Paricaud’s modeling work, gas solubility is obtained from vapor-liquid flash calculation, and the effect of TBAB on CO₂ solubility is negligible. In Paricaud’s study (and for specific conditions: at temperature=283.15 K and pressures up to 2.5 MPa) the RAD of CO₂ solubility in pure water is 6% (13 data points [294]), and CO₂ solubility in TBAB aqueous solution is 2% (6 data points [200]). Following Paricaud’s work, Fukumoto et al. [96] adjusted the temperature dependency parameter in the SAFT-VRE EOS by using solid-liquid equilibrium.
data of salt+H₂O binary systems, and applied the approach to TBAB and other SCH systems. The authors [96] stated that the solubility of CO₂ can be predicted by neglecting the dispersion interactions between ions and CO₂ molecules. Unfortunately, no details of the model performance for the solubility calculations are provided.

Ma et al. [98] applied MPT [19] to the fluid phase equilibrium of H₂O+TBAB. In MPT, chemical equilibria is considered for the CO₂+H₂O (pressures up to 1000 bar) and H₂S+H₂O systems [19], and the interaction parameter for salt-gas pairs are evaluated by fitting solubility data of gas+H₂O+salt systems under low pressures. Ma et al. [98] used vapor-liquid flash calculations to calculate gas solubility, Ma et al. [98] did not provide details of the model performance for solubility calculations.

Apart from the electrolyte EOS approach, Kwaterski and Herri [101] used the SRK plus electrolyte Non-Random Two Liquid model (e-NRTL) for aqueous TBAB solutions. They adopted Henry’s constant for calculating the ideal solubility of CH₄ in the aqueous phase. Verrett et al. [102] used the Trebble–Bishnoi EOS (TB) plus e-NRTL for the aqueous TBAB solution, and in their modeling work, the gas solubility is obtained from vapor-liquid flash calculation. Verrett et al. assumed that the gas solubility in the liquid phase is unaffected by the presence of TBAB, but they also pointed out that this assumption may be a source of error. Najibi et al. [104] utilized the Peng-Robinson EOS (PR) plus Mean Spherical Approximation for aqueous electrolytes including Ionic hydration and association (AMSA)-NRTL for aqueous TBAB solution. In Najibi et al.’ work, the solubility of CO₂ in pure H₂O and in a solution are predicted by the PR EOS and the AMSA-NRTL model respectively. Najibi et al. stated that the AMSA-NRTL model accurately predicts the salting-out effect of TBAB (mass fraction of TBAB=0.09, temperature=283.15 K) in contact with pure H₂O.

Eslamimanesh et al. [105] used the PR EOS for the vapor phase, plus NRTL for non-electrolyte compounds in the liquid phase, and they use a correlation based on the experimental data for the mean
ionic activity coefficients of the electrolyte part. Eslamimanesh et al. [105] used the Krichevsky–Kasarnovsky equation [295] to calculate gas solubility in the aqueous phase. Eslamimanesh et al. [105] stated that the effect of TBAB presence on gas solubility are relatively small. Muromachi et al. used Mao’s model [296] to correlate N₂ solubility in aqueous TBAB solution, the results show that Mao’s model can give good agreements with experimental data.
So far, the calculation of gas solubility in aqueous solutions of QAS has not been extensively studied. And only a few electrolyte EOS have been proposed for such studies. It is of interest to investigate the performance of a new electrolyte EOS for calculating gas solubility in aqueous QAS solutions, especially for aqueous TBAB solution.

4.3.1 Data analysis
Although there are a few experimental data of gas solubility in aqueous QAS solutions, the experimental data with large experimental uncertainty are not considered in this work. We compare the CO₂ solubility data from Muromachi et al. [297] and data from Lin et al. [298] at 298.15 K, the deviations between the two data sets are not too large, so the two data sets of CO₂ solubility are both included in this work. But for N₂ solubility data, the experimental uncertainties of Muromachi et al. [299] are too large (uncertainty of gas mole fraction in liquid is 0.00012, while the mole fraction of N₂ in pure water is 0.0003 at 292.15 K and 3.0 MPa), so, N₂ solubility data from Muromachi et al. [299] are not included in this work.
Modeling of Gas Solubility

(a) mass fraction of TBAB=10%

(b) mass fraction of TBAB=20%
Modeling of Gas Solubility

Figure 4.15 Comparison of experimental solubility between Muromachi et al. [297] and data from Lin et al. [298] at 298.15 K.

(a) Garzon et al.'s data [300]
Figure 4.16 Experimental uncertainties of experimental N$_2$ solubility in aqueous TBAB solution.

For the gas solubility of other gases in aqueous solutions of QAS, the experimental data are limited, and the regions of overlap of the different studies are rather narrow, thus comparisons and detailed analysis are difficult. All these data were used in the present work.

### 4.3.2 Modeling Results

In this work, the following binary systems are studied: H$_2$O+C$_2$H$_6$, H$_2$O+TMAB, H$_2$O+TEAB, H$_2$O+TPAB. Moreover, the following gas-containing ternary systems are considered: TMAB+H$_2$O+CH$_4$, H$_2$O+TMAB+C$_2$H$_6$, H$_2$O+TEAB+CH$_4$, H$_2$O+TEAB+C$_2$H$_6$, H$_2$O+TPAB+CH$_4$, H$_2$O+TPAB+C$_2$H$_6$, H$_2$O+TBAB+CO$_2$, H$_2$O+TBAB+N$_2$, H$_2$O+TBAB+CH$_4$, H$_2$O+TBAB+C$_2$H$_6$.

Table 4.7 summarizes the ion-gas interaction parameters and the performance of e-CPA for the correlation of gas solubility.
### Table 4.7 Binary ion-gas interaction parameters and performance of e-CPA on gas solubility correlation.

<table>
<thead>
<tr>
<th>Gas</th>
<th>T [K]</th>
<th>P [MPa]</th>
<th>m a</th>
<th>Np</th>
<th>Approach A</th>
<th>Approach B</th>
<th>Approach C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Δ(U_{ij}^{ref}/R)</td>
<td>(\tau_{\Delta U_{ij}})</td>
<td>(\omega_{\Delta U_{ij}})</td>
</tr>
<tr>
<td>(\text{H}_2\text{O}+\text{TMAB}+\text{gas})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[K]</td>
<td>[K]</td>
<td>[%]</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>278.15-308.15</td>
<td>0.101</td>
<td>0.176-0.302</td>
<td>7 [301]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>278.15-308.15</td>
<td>0.101</td>
<td>0.165-0.325</td>
<td>6 [301]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2\text{O}+\text{TEAB}+\text{gas})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_4)</td>
<td>278.15-308.15</td>
<td>0.101</td>
<td>0.093-1.0</td>
<td>39 [261, 301]</td>
<td>802.2</td>
<td>596.1</td>
<td>-604.3</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>278.15-308.15</td>
<td>0.101</td>
<td>0.098-0.436</td>
<td>8 [301]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2\text{O}+\text{TPAB}+\text{gas})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_4)</td>
<td>278.15-308.15</td>
<td>0.101</td>
<td>0.097-0.706</td>
<td>21 [301]</td>
<td>773.2</td>
<td>202.0</td>
<td>678.6</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>278.15-308.15</td>
<td>0.101</td>
<td>0.102-0.805</td>
<td>17 [301]</td>
<td>788.2</td>
<td>325.6</td>
<td>194.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2\text{O}+\text{TBAB}+\text{gas})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO(_2)</td>
<td>286.15-303.1</td>
<td>0.2-4.0</td>
<td>0.342-2.074</td>
<td>145 [297, 298]</td>
<td>519.7</td>
<td>896.6</td>
<td>374.5</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>278.15-308.15</td>
<td>0.101</td>
<td>0.096-4.01</td>
<td>43 [301, 302]</td>
<td>628.4</td>
<td>679.3</td>
<td>3559.0</td>
</tr>
<tr>
<td>N(_2)</td>
<td>283.15-298.15</td>
<td>0.101</td>
<td>0-1.0</td>
<td>24 [300]</td>
<td>643.5</td>
<td>499.4</td>
<td>2770.8</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>278.15-308.15</td>
<td>0.101</td>
<td>0.099-0.304</td>
<td>8 [301]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a. \(m\) is molality of salts; b. \(N_p\) is number of data points.
From Tables 4.7, it can be seen that e-CPA performs well for most systems over a wide temperature range. The approach with temperature-dependent parameters provides the best results, as might have been expected. The RAD for H₂O+TBAB+CO₂ is not that small, and this may be due to the deviations between Muromachi et al.’s data [297] and Lin et al.’s data [298]. If only do regression for Lin et al.’s data [298], the RAD is 7.5%.

In the following parts, only interaction parameters and results with Approach A are discussed for the systems which have data over a wide temperature range.

Figures 4.17-4.23 show the modeling results for metal halide salts and quaternary ammonium salts systems. CO₂ is the most studied gas in gas solubility studies in TBAB aqueous solutions. Some researchers consider that the presence of TBAB does not affect the gas solubility of CO₂ in water, Kamata et al. [303] reported that the CO₂ solubility in a solution (mass fraction of salt=0.1) were almost equal to that in pure water at atmospheric pressure. On the other hand, some researchers [297, 298] found that the presence of TBAB does affect the solubility of CO₂ in water. Figure 4.17 illustrates the model performance of CO₂ solubility in aqueous TBAB solutions.

It can be seen from Figure 4.17 that e-CPA can overall correlate well the solubility of CO₂ in aqueous TBAB solution. For CO₂ dissolution in aqueous TBAB solutions, the salt effects of TBAB on CO₂ in H₂O are complex. Lin et al. [298] stated that salting-in effect obviously exists at 298.15 K with a mass fraction of TBAB=0.4, and salting-out effect exists at 290.15 K with mass fraction of TBAB=0.2, and the CO₂ solubility in aqueous TBAB solution at 290.15 K with mass fraction of TBAB=0.4 is quite close to that in pure H₂O. Lin et al. [298] also observed that temperature increase facilitated the salting-in in mass fraction of TBAB=0.4, and salting-in effects exist at high temperature and high TBAB concentration for H₂O+TBAB+CO₂ system. From the experimental investigations, there is no explicit salting-in or salting-out effect region for TBAB on CO₂ (RAD=9.2 %).
Figure 4.17 Comparison of the modeling results against the experimental CO$_2$ solubility in aqueous TBAB solution [298].
Figure 4.18 shows the model performance of N\textsubscript{2} solubility in aqueous TBAB solution.

Figure 4.18 Comparison of the modeling results against the experimental N\textsubscript{2} solubility in aqueous TBAB solution [300].

From Figure 4.18, it can be seen that e-CPA can correlate well the high-temperature data, but the deviations are a bit larger at low temperature and low molality. TBAB shows salting-in effects on N\textsubscript{2} in water, and the salting-in effects are stronger at higher temperatures. e-CPA can correlate well the high-temperature data, but the deviations are a bit higher at low temperature and low molality.

Garzon et al. [300] found that the solubility of N\textsubscript{2} increases as the concentration increases at a certain pressure-temperature-molality range (in a concentration interval ranging from 0.2 to 1.0 mol/kg and temperatures between 283.15 K and 298.15 K, at 101.325 kPa partial gas pressure). Garzon et al. [300] stated that the salting-in effects are not caused by micelle formation.
The solubility of N\textsubscript{2} in pure water is about 1/100 of that of CO\textsubscript{2}, so, more accurate data are needed for N\textsubscript{2} solubility study. Due to the low solubility of nitrogen, and high uncertainty of the measurements, it is hard to obtain very clear salt-effects regions [300]. Muromachi et al. [297] also stated that their measurements were not accurate enough to evaluate the temperature dependency in the pure water system. Despite the low accuracy of their measurements, Muromachi et al. [299] still proposed the salting effects based on their experimental data: The aqueous TBAB solutions with mass fractions of 0.10 and 0.20 have similar N\textsubscript{2} gas solubility as that in pure water; With mass fraction of 0.32 and 0.40, TBAB has slight salting-in effects on N\textsubscript{2}.

Figure 4.19 shows the model performance of CH\textsubscript{4} solubility in aqueous solutions of TEAB, TPAB and TBAB.
Figure 4.19 Comparison of the modeling results against the experimental $\text{CH}_4$ solubility in aqueous solutions of (a) TEAB solution [261], (b) TPAB [301] and (c) TBAB [301, 302].
Overall, e-CPA gives good agreement for the CH₄ solubility. From Figure 4.19 (a), it can be seen that TEAB shows slight salting-in effects on the solubility of CH₄ in H₂O at high temperatures, and slight salting-out effects at low temperatures. From Figure 4.19 (b), it can be seen that TPAB shows salting-in effects on the solubility of CH₄ in H₂O at high temperatures, and a transition that from salting-in (lower molality) to salting-out (higher molality) at low temperatures. Similar with TPAB, from Figure 4.19 (c), it can be seen that TBAB shows slight salting-out effects at low temperatures, and shows apparent salting-in effects at high temperatures. From the experimental data of CH₄ solubility in aqueous TBAB solution, Wen and Hung’s data [301] show that the presence of TBAB increases the solubility of CH₄ at 288.15 K, 298.15 K, and 308.15 K. In the particular case of CH₄ in aqueous TBAB solutions at 278.15 K, the solubility increases slightly as the salt molality increases from 0 to 0.2 mol/kg water but then decreases with the further increase of the concentration (with salt molality increases from 0.2 to 1.0 mol/kg water). The two CH₄ [301, 302] data sets show opposite effects in that, Wen and Hung’s results [301] show a decrease in salting-in, but Feillolay and Lucas [302] show an increase in salting-in as the electrolyte molality increases.

The data from Wen and Hung and Feillolay and Lucas have been used in the regression. TBAB shows larger salting-in effects at high salt molality than low molality. The e-CPA equation of state cannot represent well the salting-in effects at high salt molality [302].

There are only a few scatter data of the solubility C₂H₆ in most aqueous solutions, except for C₂H₆ in aqueous TPAB solutions. Figure 4.20 shows the model performance of C₂H₆ solubility in aqueous TPAB solution.
Figure 4.20 Comparison of the modeling results against the experimental \( \text{C}_2\text{H}_6 \) solubility in aqueous TPAB solution [301].

Figure 4.21 Comparison of the modeling results against the experimental \( \text{N}_2 \) solubility in aqueous solutions of NaCl and TBAB [300] at \( P=101325 \) Pa and \( T=298.15 \) K.
Figure 4.22 Comparison of the modeling results against the experimental CO$_2$ solubility in aqueous solutions of NaCl [274] and TBAB [297] at 298.15 K.

Figure 4.23 Comparison of the modeling results against the experimental C2H6 solubility in aqueous solutions of NaCl [304] and QAS [301].
From Figure 4.20, it can be seen that e-CPA can correlate well the solubility of C$_2$H$_6$ in aqueous TPAB solution. TPAB shows slight salting-in effects on C$_2$H$_6$ in water, and the effects become stronger at high temperatures. Different salts have different salt effects on gas solubility and Figures 4.21-4.23 illustrate visually the different effects.

From Figures 4.21-4.23, it can be seen that, the presence of NaCl can decrease gas solubility in water, while the salt effects of QAS on gas are complex with different temperature, pressure, and salt concentration, and there is no clear salting-in effect and salting-out effect regions. A general trend is that salting-in effects will appear at high temperature, pressure and QAS concentration.

### 4.3.3 Discussion

#### 4.3.3.1 Salting-in Effects

The presence of QAS has complex effects on gas dissolution in water and some researchers have proposed explanations for these effects. Similar with ion hydration of normal ions, Wen and Hung [301] proposed ‘cage effect’ theory (R$_4$N$^+$ hiding in the water molecular cage) to explain the salting-out effects of R$_4$N$^+$ on gas. They stated that this cage is not for the small solutes but for hiding the hydrocarbon chain of R$_4$N$^+$ ions. Based on Monte Carlo simulations, Hribar et al. [184] found that the TMA$^+$ structure allows deep penetration by a first shell of waters, and this first water shell sets up a second water shell, these two shells shaped to act as a receptacle which can bind the nonpolar solute. Hribar et al. [184] stated that this is the main reason for salting-in effects of TMA$^+$.

For the dissolution of CO$_2$ in aqueous TBAB solutions, Lin et al [298] concluded that there is a competition between two opposite trends with temperature and TBAB concentration change. TBAB
reorganizes the water molecule to accommodate more CO\textsubscript{2} molecules or enhances the water structure (cage effect) \cite{305} thereby repelling CO\textsubscript{2}. Lin et al. \cite{298} stated that the ‘reorganizing effect’ seemed to be important at a higher temperature (at 298.15 K), while the ‘cage effect’ of water becomes important at lower temperatures (at 290.15 K). Moreover, lower TBAB concentration (mass fraction of TBAB=0.2) showed lower reorganizing ability and thereby resulting in salting-out for CO\textsubscript{2} at 290.15 K and 293.15 K. At a certain temperature and TBAB concentration, these two competing factors might have similar contributions, which cancel out the salinity effect on CO\textsubscript{2} solubility, as exemplified for the mass fraction of TBAB=0.40 at T=293.1 K, and the mass fraction of TBAB=0.20 and T=303.1 K.

For CH\textsubscript{4} solubility study, Lin et al. \cite{298} applied the ‘cage effect’ \cite{301} to explain the salting-out effect of TBAB on CH\textsubscript{4}, which was observed at 278.1 K and mass fraction of TBAB=0.11 to 0.20.

Lin et al. \cite{298} did not provide a clear explanation of ‘disorganization of water molecule’. Here, we treat this ‘disorganization effect’ similar with the Hribar et al.’ theory \cite{184}, and we name it as ‘disorganization effect’.

In this work, the influence factors of gas solubility in TBAB aqueous solution can be summarized in four main aspects, the details are listed in Table 4.8.

The dissolution of gas in aqueous QAS solution is complex; the gas dissolution depends on temperature, pressure, salt concentration, organic cation and gas molecule. Hydrophobic effect plays an important role in gas dissolution.

As for the effects on hydrate formation, gas solubility is just one factor. Su et al.\cite{92} and Gupta et al. \cite{93} observed that TBAB is a hydrate promoter, but TPAB, TEAB and TMAB are hydrate inhibitors. Nguyen and Nguyen \cite{94} explained that the hydrophobic part of quaternary ammonium salts (organic cation) acts as a hydrate promoter, while the hydrophilic part (anion) acts as a hydrate inhibitor. It creates two competitive effects on gas hydrate
formation, the effects of salt depend on which effect is dominant in the working condition. Obviously, TBAB has longer hydrocarbon chains and therefore is more hydrophobic in comparison with TPAB, TEAB, and TMAB.

Table 4.8 A summary of salt effects of QAS on gas in water.

<table>
<thead>
<tr>
<th>No</th>
<th>Effects</th>
<th>Ions</th>
<th>Theory</th>
<th>Influence Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Salting-out</td>
<td>Anion</td>
<td>Ion hydration</td>
<td>Weakens with increasing temperature;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[184]</td>
<td>Enhances with increasing salt molality</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>‘cage effect’ [301]</td>
<td>Weakens with increasing temperature;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>‘disorganization effect’ [184]</td>
<td>Enhances with increasing temperature and salt molality</td>
</tr>
<tr>
<td>4</td>
<td>Salting-in</td>
<td>Cation</td>
<td>‘hydrophobic bond’ [306, 307]</td>
<td>Enhances with increasing temperature</td>
</tr>
</tbody>
</table>

4.3.3.3 Model Suitability

Actually, there are only two electrolyte EOS which have been applied for gas solubility in aqueous QAS solutions: SAFT-VRE [21] and MPT [98], and only MPT [98] takes into account the effects of QAS on gas. Ma et al. [98] used a vapor-liquid flash algorithm to calculate gas solubility, while they did not provide the details of the performance of modeling the gas solubility in aqueous solutions. Though some activity coefficient models can perform well for gas solubility calculation in aqueous solutions of QAS, the temperature and molality ranges are narrow. e-CPA takes into account ion hydration, and introduces a new
model for the static permittivity calculation, which can eliminate the kinetic effects from kinetic depolarization. The cations of QAS are soft and with long alkyl chains. In order to obtain more physical cation radii, in this presented e-CPA approach, the cation diameters of QAS are first fitted to experimental data of mean ionic activity coefficients and osmotic coefficients of aqueous solutions of QAS. From the above, the salt effects of QAS on gas are complex, and should not be ignored, especially at high temperature and salt concentration. In this work, we take into account the interaction between ions and gas, and we consider temperature-dependence for the interaction parameters. The temperature-dependence is very important in this case, because the salt effects of QAS are different at different temperatures.

e-CPA shows some limitations. For instance, it cannot reflect the complex salt effects of QAS on the solubility of gas in H₂O. A potential solution could be taking the hydrophobic effects into account in the model.

4.3.4 Conclusion

This section presents a theoretical study on the thermodynamic modeling for aqueous solutions of quaternary ammonium salts (QAS) by using the e-CPA EOS, which includes the Debye–Hückel and Born terms for electrostatic contributions. The representation of gas solubility in aqueous QAS solutions is challenging, as the cations of QAS have large alkyl chains and low charges, thus exhibiting hydrophobic-like character. Another reason is that the salt effects of gas-QAS systems are complex and these effects come from different competing factors which depend on temperature and salt concentration. The cation size of QAS and the temperature-dependent ion-solvent interaction parameters are estimated from mean ionic activity coefficients and osmotic coefficients. e-CPA provides good agreement with experimental data of water-QAS binary systems. The temperature-dependent
ion-gas interaction parameters are estimated from gas solubility in aqueous solutions and using these parameters e-CPA yields successful correlation results for gas solubilities. Adding dissociation equilibrium to the model is a potential solution for organic salt solutions where ion-pairs and hydrophobic effects exist. In order to provide a detailed analysis for salt effects of QAS on gas, more accurate experimental data are needed (several gases in aqueous solutions of TMAB, TEAB, TPAB, and N₂, C₂H₆ in aqueous TBAB solution).
Chapter 5. Modeling the Activity Coefficients of Individual Ions in Aqueous Solutions

This chapter presents modeling study of activity coefficients of individual ions in aqueous solutions using various electrolyte models, as well as a discussion including an analysis of the terms from the various modeling approaches.

Chapter structure and contents:
5.1 Thermodynamic Equations and models considered
5.2 Database and parameter estimation
5.3 Results
5.4 Discussion
5.5 Conclusion
Abstract
The investigation of individual ion activities is important for research of mineral and biological systems as well as for the validation of models for electrolyte solutions. This work presents a modeling study of individual ion activities in aqueous solutions of several inorganic salts with the electrolyte Cubic-Plus-Association Equation of State (e-CPA) and other approaches including the ‘extended version of Debye–Hückel + Born’ model, and the ‘MSA+Born’ model. The results with the various approaches are not identical with the ‘extended version of Debye–Hückel + Born’ model performing overall better. The study shows that, while good results are obtained in many cases, several parameters like the ion radius, Born radius and dielectric constant have a significant effect on the results.

Introduction
Over a long time, the investigation of individual ion activities has attracted considerable attention [308, 309]. This is because activity coefficients of individual ion can be useful in the characterization of transport phenomena in electrolyte systems [310, 311] and are also helpful in our understanding of biological systems (sodium–potassium pump), membrane processes, as well as salting-in and salting out effects [309, 312]. Moreover, recently, in some modeling studies, individual ion activities have been considered, as discussed below.

The usual experimental method for individual ion activities is via electrochemical cell measurements using ion-selective electrodes (ISE) and liquid junction potential [313], then applying expressions for the junction potential and Electromotive force (EMF) of the ISE related to the ionic activities [312, 314-316]. The experimental data of activity coefficients of individual ions published in literature are presented in Table B.1 of Appendix for several inorganic salts. Below we discuss some of the modelling studies where such data
are used.
Fraenkel [313] used for modelling MC-UPM (Monte Carlo simulations of the unrestricted PM) and DH–SiS (extension of the DH theory for the case of ions of unequal size). In their modeling work [313], selected salts (LiCl, NaCl, NaBr, MgCl₂, CaCl₂, K₂SO₄) in aqueous solutions are studied. Besides system variables and universal constants, only the size of the ion and the closest distance of the ion to its counterion are necessary individual factors in evaluating the single-ion activity. They stated that there is no need to consider ion solvation, ion pairing, and core effects in computing single-ion activities, if what is desired is a simplified correlation between theory and experiment.

Liu [317] proposed the Poisson-Fermi model. In this model, the steric effect of water molecules and interstitial voids in the first and second hydration shells play an important role, and the screening and polarization effects of water are also included in the model. Liu and Eisenberg [317] applied this model to calculate the activity coefficients of individual ions in electrolyte solutions with any arbitrary number of ionic species (NaCl and CaCl₂ in aqueous solutions) in a large range of salt concentrations and temperatures. The Poisson-Fermi model gives good agreement with experimental data.

Valiskó et al [44, 58, 318, 319] proposed the so-called ‘ion-ion (II)+ion-water (IW)’ (II+IW) theory. The II term was computed from grand canonical Monte Carlo (GCMC) simulations [320], and the IW term was computed from the Born equation [26]. Valiskó et al [44, 58, 318, 319] applied this theory for the calculation of activity coefficients of individual ions in aqueous solutions of several inorganic salts. The results show good agreement with experimental data for activity coefficients of individual ion of several salts in aqueous solutions.

Valiskó and Boda applied the extended version of Debye-Hückel (EDH) model [42] for aqueous solutions of NaCl and CaCl₂ [321]. Valiskó and Boda [58] mentioned that the mean spherical approximation (MSA) [29] can also be used as an alternative
method for calculating the II term.
In this work, in addition to some of the aforementioned models, the electrolyte Cubic-Plus-Association (e-CPA) EOS proposed by Maribo-Mogensen et al. [24] is also used. The rest of the chapter is organized as follows: firstly, the basic thermodynamic equations and the thermodynamic models considered will be presented. Then the modeling results will be shown with all approaches, together with an analysis of the various contributions, discussion of the results and finally our conclusions.

5.1 Thermodynamic Equations and models considered

A salt dissociates into νC cations C, and νA anions A with ionic charges Z_C and Z_A. The Greek letter ν is the sum of the stoichiometric coefficients:
\[ ν = νC + νA \] (5.1)
The molality \( m_i \) of an ion \( i \) is the number of moles \( n_i \), of the ion per kg water in the liquid phase.
The mole fraction of water \( x_w \) is:
\[ x_w = \frac{n_w}{n_w + \sum n_{ion_k}} = \frac{\frac{1000}{M_w}}{\frac{1000}{M_w} + \sum m_k} \] (5.2)
Where, \( n_w \) is the mole numbers of solvent (water), \( n_{ion_k} \) is the mole numbers of ion \( k \), \( M_w \) is the molecular weight of the solvent (water in this work), and \( m_k \) is the molality of ion \( k \) and the sum is over all ions present.
The molality (based) activity coefficient is defined:
\[ \ln γ_i^m = \ln(x_wγ_i^*) = \ln γ_i^* - \ln[1 + 0.001M_w\sum m_k] \] (5.3)
\( γ_i^* \) is the rational, unsymmetrical activity coefficient of component \( i \) (cation, anion).
The mean molal activity coefficient is defined:
\[ γ_±^m = (γ_C^m)^{νC}(γ_A^m)^{νA})^{1/ν} \] (5.4)
Chemical potentials were derived from the energy function by
molar differentiation at constant temperature and volume [1]:

$$\mu_i^{EX} = \left[ \frac{\partial A_i^{EX}}{\partial n_i} \right]_{T,V,n_j}$$  \hspace{1cm} (5.5)

The excess chemical potential for component $i$ is:

$$\mu_i^{EX} = RT \ln \gamma_i^*$$  \hspace{1cm} (5.6)

Here, $\gamma_i^*$ is the activity coefficient (rational) of ion $i$.

Table 5.1 summaries the free energy contributions from the different models considered here, while a short description follows. Valiskó et al [44, 58, 318, 319, 321] proposed the II+IW theory in which they split the excess chemical potential into two parts:

$$\mu_i^{EX} = \mu_i^{EX,II} + \mu_i^{EX,IW}$$  \hspace{1cm} (5.7)

where the II and IW terms describe the ion–ion and ion–water interactions, respectively (subscript $I$ refers to an ionic species).

In Valiskó et al’s work [44, 58, 318, 319, 321], the II term was computed from Grand Canonical Monte Carlo (GCMC) simulations, or alternatively the extended version of Debye-Hückel (EDH) [42] (only for aqueous solutions of NaCl and CaCl$_2$ [321]) theory can also be used for the II calculation [319]. The IW term for ion solvation is calculated by the Born equation [26].

Shilov and Lyashchenko [42] extended the Debye–Hückel theory to allow for arbitrary concentration dependence of the electrolyte solution static permittivity. MSA can also be used as an alternative method for the II term [58].

It should be noted that, in the II+IW theory, experimental volume and dielectric constant for aqueous electrolyte solutions (concentration-dependent values) should be used [58]. In Valiskó et al’s work [44, 58, 318, 319, 321], the II term is computed using hard sphere ions with Pauling radii. The IW term is computed using Born radius, which they fitted from the hydration free energy.

Maribo-Mogensen et al. [24] extended the CPA EOS, which was proposed by Kontogeorgis et al. [25] to mixtures containing electrolytes. Maribo-Mogensen et al. [24] published the adjustable model parameters for several salts which are used unchanged
Modeling the Activity Coefficients of Individual Ions in Aqueous Solutions

here.

In this work, the DH term (e-CPA), EDH term and MSA term are all used in II+IW theory calculations. In addition to differences in expression, the values of inverse Debye screening length (κ) and ion radius in calculation (rcal,i) are the apparent differences between the different II terms. MSA and e-CPA use the inverse Debye screening length related to the static permittivity of solution, EDH uses the inverse Debye screening length related to the static permittivity of water (with no salt). The DH term (e-CPA) uses individual ion radius for individual ion calculations, while EDH and MSA use average ion radius.

Table 5.1 The calculation of II (ion-ion) term in different models as well as the and IW (ion hydration) term.

<table>
<thead>
<tr>
<th>Term</th>
<th>Model</th>
<th>Contribution</th>
<th>κ *</th>
<th>rcal,i</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>e-CPA [24]</td>
<td>( A^{DH} = -\frac{k_BT V}{4\pi N_A \sum_i n_i Z_i^2} \sum_i n_i Z_i^2 \chi_i ) Eq. (2.4)</td>
<td>( \kappa )</td>
<td>( r_i )</td>
</tr>
<tr>
<td>II</td>
<td>EDH [42]</td>
<td>( G^{DH} = -\frac{k_BT V}{12\pi \kappa_0^3} \tau_1(\kappa_0, a) )</td>
<td>( \kappa_0 )</td>
<td>( a/2 )</td>
</tr>
<tr>
<td>II</td>
<td>MSA [29]</td>
<td>( A^{DH} = -\frac{2\Gamma^3 RTV}{3\pi N_A} \left( 1 + \frac{3}{2} \Gamma_{MSA} \sigma \right) ) Eq. (2.20)</td>
<td>( \sigma )</td>
<td>( \sigma^* )</td>
</tr>
<tr>
<td>IW</td>
<td>Born [26]</td>
<td>( G^{Born} = \frac{Z^2 e^2}{8\pi \varepsilon_0 r_{Born,i}} \left[ \frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_w} \right] )</td>
<td></td>
<td>( r_{Born,i} )</td>
</tr>
</tbody>
</table>

*. inverse Debye length; +. average diameter \( \sigma \) in MSA (Eq. (2.18)).

In Table 5.1, \( A^{DH} \) is II contribution of residual Helmholtz energy, \( G^{DH} \) is the II contribution of Gibbs free energy, \( G^{Born} \) is the IW contribution of Gibbs free energy. \( V \) is the total volume, \( k_B \) is the Boltzmann constant, \( N_A \) is the Avogadro constant, \( Z_i \) is the charge of component \( i \), \( \kappa \) is the inverse Debye screening length, \( \kappa_0 \) is the usual inverse Debye length, defined by inverse Debye length with the use of pure solvent static permittivity of solution, \( d_i \) is the hard-sphere diameter of the ion, \( a \) is the distance of closest approach which was assumed to be the sum of the ionic radii, \( a = r_{cation} + r_{anion} \), \( r_{Born,i} \) is Born radius of ion \( i \), \( e \) is the electronic
charge \((1.60206^{-19} \text{ C})\), \(\varepsilon_0\) is the permittivity in vacuum \((8.8542^{-12} \text{ C}^2/\text{J/m})\), \(\varepsilon_r\) is the relative static permittivity of the solvent, \(\varepsilon_w\) is the relative static permittivity of the solvent (with no salt).

In e-CPA, the function \(\chi_i\) is given by:

\[
\chi_i = \frac{1}{d_i^3} \left[ \ln(1 + \kappa d_i) - \kappa d_i + \frac{1}{2} (\kappa d_i)^2 \right] \quad (5.8)
\]

where \(\kappa\) is the inverse Debye screening length, and \(d_i\) is the hard-sphere diameter of the ion \(i\).

In EDH, the expression for the ion-ion interaction contribution to activity coefficient of ion is obtained:

\[
\ln \gamma_i^* = -\frac{Z_i^2 e^2 \kappa_0 \chi_1(\kappa_0, a)}{3kT\varepsilon_w} + \frac{\bar{V}_i \kappa_0^3 \sigma_1(\kappa_0, a)}{24\pi N_A} \quad (5.9)
\]

Where \(\bar{V}_i\) is the partial molar volume of ion \(i\). In this calculation, we eliminate the second part of right part in Eq. (5.9).

In EDH, \(\kappa_0\) is the usual inverse Debye length, defined with the use of pure solvent static permittivity of solution:

\[
\kappa_0^2 = \frac{4\pi e^2}{\varepsilon_w kT V} \sum_i n_i Z_i^2 \quad (5.10)
\]

Where, \(n_i\) is the mole number of ion \(i\), \(V\) is the total volume of solution.

The function \(\tau_1(\kappa_0, a)\):

\[
\tau_1(\kappa_0, a) = 3 \int_0^1 \frac{\lambda^2}{f(\kappa_0 \lambda)(\sqrt{f(\kappa_0 \lambda)} + \kappa_0 a \lambda)} d\lambda \quad (5.11)
\]

In MSA, the average diameter \(\sigma\) is:

\[
\sigma = \frac{\sum_{\text{ions}} n_i \sigma_i}{\sum_{\text{ions}} n_i} \quad (5.12)
\]

\(\Gamma_{\text{MSA}}\) is given with an implicit expression:
Modeling the Activity Coefficients of Individual Ions in Aqueous Solutions

\[ \Gamma_{MSA} = \frac{1}{2\sigma} \left[ \sqrt{1 + 2\sigma \kappa} - 1 \right] \]  
(5.13)

1/\kappa is a characteristic length called the screening length, and is identical to the expression used in Debye-Hückel theory:

\[ \kappa = \left( \frac{e^2 N_A^2}{\varepsilon_r \varepsilon_0 RT V \sum_{i \text{ions}} n_i Z_i^2} \right)^{1/2} \]  
(5.14)

5.2 Database and parameter estimation

There is significant debate in literature about the concept of activity coefficients of individual ions and the obtained experimental data. In order to evaluate the experimental data, we calculated the mean ionic activity coefficients from activity coefficients of individual ions, and compare these calculated values with the experimental mean ionic activity coefficients from literature (obtained from direct measurements or via osmotic activity coefficients). Figure B.1 of Appendix show a preliminary evaluation for 9 salts. It can be seen from these figures that the deviations between different data sets are small, and the deviations of mean ionic activity coefficients between calculated values (from single ion data) and the actual experimental data are also small. While this is not an ultimate proof of the correctness of the single ion values, it is a good indication and we proceed with the use of activity coefficients of individual ions.

The experimental results show that the activity coefficients are different for the anion and the cation in an aqueous solution. For the individual ionic activities of Na+, the values in aqueous solutions of NaF, NaCl and NaBr are different, because the individual ionic activities are affected by the interaction of cation and anion. Similarly, for the individual ionic activities of Cl⁻ in aqueous solutions of NaCl and KCl. Figure B.2 of Appendix show the individual ion activity coefficients of Na⁺ and Cl⁻ in different aqueous electrolyte solutions.

In this work, we study 9 salts: 1:1 electrolytes (NaCl: sodium
chloride, KCl: potassium chloride, NaBr: sodium bromide, NaF: sodium fluoride); 2:1 electrolytes (CaCl$_2$: calcium chloride, MgCl$_2$: magnesium chloride); 1:2 electrolytes (Na$_2$SO$_4$: sodium sulfate, K$_2$SO$_4$: potassium sulphate); 3:1 electrolytes (LaCl$_3$: lanthanum chloride).

Water-ion interaction parameters in e-CPA, ion radii, Born radii of several inorganic salts can be found in Tables 3.2, 3.3.

The density of aqueous electrolyte solutions as a function of their temperature and concentration can be expressed as [322]:

$$\rho = \rho_w + Ac + Bct + Cct^2 + Dc^{3/2} + Ec^{3/2}t + Fc^{3/2}t^2$$  \hspace{1cm} (5.15)

where A through F are adjustable constants (listed in Table 5.2), $c$ is the salt concentration in mol/L, $t$ is the temperature in °C, and $\rho$ is the density of solution in kg/m$^3$. The density of water, $\rho_w$ is calculated according to the empirical equation [322]:

$$\rho_w = 999.65 + 2.0438 \times 10^{-1}t - 6.174 \times 10^{-2}t^{3/2}$$  \hspace{1cm} (5.16)

Table 5.2 Parameters for correlation of liquid densities of aqueous electrolyte solutions (from literature [322]).

<table>
<thead>
<tr>
<th>Salt</th>
<th>$A \times 10^{-2}$</th>
<th>$-B \times 10$</th>
<th>$C \times 10^3$</th>
<th>$-D$</th>
<th>$E \times 10^2$</th>
<th>$-F \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.4485</td>
<td>9.9634</td>
<td>0.6136</td>
<td>2.712</td>
<td>1.009</td>
<td>0</td>
</tr>
<tr>
<td>KCl</td>
<td>0.4971</td>
<td>0.7150</td>
<td>0.6506</td>
<td>2.376</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NaBr</td>
<td>0.8362</td>
<td>1.872</td>
<td>1.353</td>
<td>2.847</td>
<td>4.791</td>
<td>3.413</td>
</tr>
<tr>
<td>NaF</td>
<td>0.4940</td>
<td>2.985</td>
<td>3.365</td>
<td>4.752</td>
<td>16.22</td>
<td>18.72</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>1.012</td>
<td>61.56</td>
<td>1.028</td>
<td>9.749</td>
<td>96.94</td>
<td>3.165</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>0.8099</td>
<td>1.887</td>
<td>2.3156</td>
<td>6.029</td>
<td>7.449</td>
<td>8.305</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>1.412</td>
<td>4.535</td>
<td>3.766</td>
<td>17.51</td>
<td>21.11</td>
<td>17.73</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>1.619</td>
<td>7.181</td>
<td>5.994</td>
<td>34.81</td>
<td>77.97</td>
<td>61.85</td>
</tr>
<tr>
<td>LaCl$_3$</td>
<td>2.319</td>
<td>0.8064</td>
<td>1.110</td>
<td>13.20</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

For static permittivity of solvent in aqueous electrolyte solutions, the equations of fitted curves are:

$$\varepsilon(c) = 78.45 - \delta_sc + bs c^{3/2}$$  \hspace{1cm} (5.17)

For 2:1 electrolytes, the values $\delta_s = 34$ and $b_s = 10$ are used [323]. For aqueous solutions of Na$_2$SO$_4$ and K$_2$SO$_4$, the correlations of static permittivity have been carried out in this work.
Modeling the Activity Coefficients of Individual Ions in Aqueous Solutions

and the parameters are listed in Table 5.3.

Table 5.3 Parameters for correlation of static permittivity of solvent for aqueous electrolyte solutions (from literature) [43, 44, 323].

<table>
<thead>
<tr>
<th>Salt</th>
<th>$\delta_s$ [mol$^{-1}$]</th>
<th>$b_s$ [mol$^{3/2}$]</th>
<th>$c_{max}$ $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>16.2</td>
<td>3.1</td>
<td>4.0 [43]</td>
</tr>
<tr>
<td>KCl</td>
<td>14.7</td>
<td>3.0</td>
<td>4.0 [43]</td>
</tr>
<tr>
<td>NaBr</td>
<td>20.0</td>
<td>5.0</td>
<td>4.0 [44]</td>
</tr>
<tr>
<td>NaF</td>
<td>15.45</td>
<td>3.76</td>
<td>4.0 [44]</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>30.1</td>
<td>9.6</td>
<td>1.2 [323]</td>
</tr>
<tr>
<td>K$_2$SO$_4$$^a$</td>
<td>21.3</td>
<td>5.77</td>
<td>1.0 $^b$</td>
</tr>
<tr>
<td>LaCl$_3$</td>
<td>46.48</td>
<td>8.21</td>
<td>1.0 [58]</td>
</tr>
</tbody>
</table>

$^a$ the maximum concentration (mol/L) of application of Eq. (5.17); b. fitted in this work, K$_2$SO$_4$ [324].

In this chapter, the temperature of all modeling works is 298.15 K. Table B.1 in appendix lists the molality range and number of data points of experimental data in this work.

5.3 Modeling Results

5.3.1 Results using the II+IW theory

At first, we present calculation results using the II+IW theory and various ways to estimate the II and IW contributions. In this section, the II term is calculated from EDH (as shown in Table 5.1, proposed by Shilov and Lyashchenko [42]), MSA (as shown in Table 5.1, proposed by Lebowitz and Percus [29]), and from in e-CPA. The IW term is calculated from Born equation [26] (see Table 5.1), which was proposed by Born.

Here, we follow Valiskó et al’s approach [44, 58, 318, 319, 321] using the experimental correlations of density and dielectric
constant for aqueous electrolyte solutions, and using Pauling radii in II term calculation, and Born radii in IW term calculation. Because in Valiskó et al’s works [44, 58, 318, 319], no Born radius of SO$_4^{2-}$ is available we have used the values of ion radius and Born radius from Maribo-Mogensen et al. [24]. Table 5.4 summarizes the results as average absolute deviations between the experimental data and predicted values from different models. It can be seen some deviations seem large for some systems, one reason being that the values of some activity coefficients are small. Overall the agreement is often satisfactory, which is a rather impressive result considering that the results are predictive, and moreover the model ignores all physical interactions.
Table 5.4 Modeling performance of different approaches for activity coefficients of individual ions.

<table>
<thead>
<tr>
<th>Salt</th>
<th>EDH</th>
<th>MSA</th>
<th>e-CPA</th>
<th>Max m</th>
<th>Np</th>
<th>EDH</th>
<th>MSA</th>
<th>e-CPA</th>
<th>Max m</th>
<th>Np</th>
<th>EDH</th>
<th>MSA</th>
<th>e-C PA</th>
<th>Max m</th>
<th>Np</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>4.4</td>
<td>9.8</td>
<td>8.6</td>
<td>3.0</td>
<td>23</td>
<td>1.7</td>
<td>2.1</td>
<td>3.5</td>
<td>3.0</td>
<td>23</td>
<td>2.8</td>
<td>5.5</td>
<td>3.7</td>
<td>3.0</td>
<td>23</td>
</tr>
<tr>
<td>KCl</td>
<td>10.6</td>
<td>4.3</td>
<td>7.7</td>
<td>3.0</td>
<td>23</td>
<td>4.1</td>
<td>5.5</td>
<td>3.0</td>
<td>3.0</td>
<td>23</td>
<td>3.8</td>
<td>1.4</td>
<td>3.6</td>
<td>3.0</td>
<td>23</td>
</tr>
<tr>
<td>NaBr</td>
<td>1.2</td>
<td>7.5</td>
<td>6.2</td>
<td>3.0</td>
<td>23</td>
<td>2.8</td>
<td>2.0</td>
<td>1.8</td>
<td>3.0</td>
<td>23</td>
<td>1.4</td>
<td>4.8</td>
<td>2.8</td>
<td>3.0</td>
<td>23</td>
</tr>
<tr>
<td>NaF</td>
<td>1.9</td>
<td>4.2</td>
<td>2.9</td>
<td>1.0</td>
<td>7</td>
<td>3.4</td>
<td>3.2</td>
<td>5.0</td>
<td>1.0</td>
<td>7</td>
<td>1.9</td>
<td>0.8</td>
<td>1.8</td>
<td>0.983</td>
<td>11</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>10.5</td>
<td>14.4</td>
<td>18.3</td>
<td>0.955</td>
<td>20</td>
<td>11.2</td>
<td>4.2</td>
<td>5.3</td>
<td>3.0</td>
<td>15</td>
<td>24.5</td>
<td>23.8</td>
<td>26.1</td>
<td>3.0</td>
<td>30</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>48.2</td>
<td>56.4</td>
<td>69.1</td>
<td>3.0</td>
<td>15</td>
<td>19.1</td>
<td>11.6</td>
<td>2.0</td>
<td>3.0</td>
<td>15</td>
<td>37.7</td>
<td>27.7</td>
<td>53.4</td>
<td>3.0</td>
<td>20</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>38.5</td>
<td>8.1</td>
<td>19.5</td>
<td>3.0</td>
<td>15</td>
<td>83.7</td>
<td>51.5</td>
<td>409.7</td>
<td>2.0</td>
<td>7</td>
<td>49.4</td>
<td>4.0</td>
<td>88.3</td>
<td>3.0</td>
<td>12</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>8.4</td>
<td>0.8</td>
<td>6.4</td>
<td>0.69</td>
<td>11</td>
<td>39.5</td>
<td>25.3</td>
<td>67.8</td>
<td>0.69</td>
<td>11</td>
<td>21.8</td>
<td>7.1</td>
<td>29.5</td>
<td>0.7</td>
<td>7</td>
</tr>
<tr>
<td>LaCl₃</td>
<td>77.2</td>
<td>75.6</td>
<td>85.7</td>
<td>1.4</td>
<td>7</td>
<td>18.0</td>
<td>18.4</td>
<td>22.8</td>
<td>1.4</td>
<td>7</td>
<td>43.2</td>
<td>24.7</td>
<td>33.9</td>
<td>1.4</td>
<td>7</td>
</tr>
<tr>
<td>Overallᵇ</td>
<td>22.3</td>
<td>20.1</td>
<td>24.9</td>
<td>-</td>
<td>-</td>
<td>20.4</td>
<td>13.8</td>
<td>57.9</td>
<td>-</td>
<td>-</td>
<td>20.7</td>
<td>11.1</td>
<td>27.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Overallᶜ</td>
<td>15.5</td>
<td>7.0</td>
<td>9.9</td>
<td>-</td>
<td>-</td>
<td>12.5</td>
<td>9.0</td>
<td>6.2</td>
<td>-</td>
<td>-</td>
<td>20.7</td>
<td>11.1</td>
<td>14.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a. outliers (≥ 50), EDH: SO₄²⁻/Na₂SO₄, La³⁺/LaCl₃; MSA: Mg²⁺/MgCl₂, SO₄²⁻/Na₂SO₄, La³⁺/LaCl₃; e-CPA: Mg²⁺/MgCl₂, SO₄²⁻/Na₂SO₄, SO₄²⁻/K₂SO₄, La³⁺/LaCl₃, MgCl₂, Na₂SO₄; b. average deviations with all deviations; c. average deviations without outliers.
Figures 5.1-5.4 present results for 1:1 electrolyte solutions. We can see that the II+IW theory (all the three models) provides good results for the individual ionic activities as well as for the mean ionic activity coefficients. At high salt molality, the deviations between experimental data and calculated values are a little larger, but overall the performance is satisfactory even at rather high concentrations.

For 1:1 electrolyte systems, all the three models perform well, especially for activity coefficients of anion and mean ionic activity coefficients. The EDH+Born performance is a little better than the other two models for activity coefficients of cation. From these results, the reproduction of the mean ionic activity coefficients, looks as good as the predictions of individual ionic activity coefficients for 1:1 electrolytes.

The Born and II terms (either DH or MSA) have big ‘opposing’ terms which become even more pronounced at high concentrations. It appears that both play an important role in the representation of the electrostatic effects for electrolyte solutions. Despite the differences mentioned above, all models appear to perform (at least from a qualitative point of view) rather similarly and there are rather small differences even between DH and MSA (although these differences are higher for cations (rather than for anions). Overall, we see a satisfactory performance also for activity coefficients of individual ions, especially considering that the results are predictive. The above qualitative picture is similar for all 1:1 electrolyte solutions considered.
Modeling the Activity Coefficients of Individual Ions in Aqueous Solutions

a. activity coefficients of cation [314]

b. activity coefficients of anion [314]
c. mean ionic activity coefficients [314]

Figure 5.1 Model performance of activity coefficients for electrolyte solution of NaCl.
b. activity coefficients of anion [314]

c. mean ionic activity coefficients [314]

Figure 5.2 Model performance of activity coefficients for electrolyte solution of NaBr.
Modeling the Activity Coefficients of Individual Ions in Aqueous Solutions

a. activity coefficients of cation [312]

b. activity coefficients of anion [312]
c. mean ionic activity coefficients [325]

Figure 5.3 Model performance of activity coefficients for electrolyte solution of NaF.

a. activity coefficients of cation [314]
Modeling the Activity Coefficients of Individual Ions in Aqueous Solutions

b. activity coefficients of anion [314]

c. mean ionic activity coefficients [314]

Figure 5.4 Model performance of activity coefficients for electrolyte solution of KCl.
As shown in figures 5.5 and 5.6, for 2:1 electrolyte systems, the EDH+Born performance is better than the other two models for activity coefficients of cation. For activity coefficient of Cl⁻ and both for CaCl₂ and MgCl₂, the performance of EDH is worse than MSA+Born and II+IW (e-CPA). Still, the differences between the various modeling approaches are rather small (both for single ion and even for mean ionic activity coefficients) and the same qualitative conclusions as for 1:1 salts also apply here e.g. about the large opposing trends of Born and DH/MSA terms. As e-CPA and EDH use essentially the same ion-ion term, the differences between these two approaches illustrate the effect that different parameters like values of ionic radii have on the results. It needs to point that, the activity coefficients of Cl⁻ back calculated from experimental activity coefficients of Ca²⁺ have big deviations with the experimental activity coefficients of Cl⁻.

![Diagram showing activity coefficients of cation](image)

a. activity coefficients of cation [326]
b. activity coefficients of anion [312]

c. mean ionic activity coefficients [61]

Figure 5.5 Model performance of activity coefficients for electrolyte solution of CaCl$_2$. 
Modeling the Activity Coefficients of Individual Ions in Aqueous Solutions

**a. activity coefficients of cation [312]**

**b. activity coefficients of anion [312]**
c. mean ionic activity coefficients [62]

Figure 5.6 Model performance of activity coefficients for electrolyte solution of MgCl$_2$.

For 1:2 electrolyte systems (Figures 5.7 and 5.8), the performance of MSA+Born is much better that that of the other two models. The II+IW version from e-CPA performs overall worse than the other two models. Clearly in this case we see a larger difference between the modelling approaches. For the e-CPA and EDH models, it appears that the ionic term is alone rather close to single ion data, resulting (when the Born term is added) to significant deviations. The differences between the models, and thus the deviations from experimental data, are smaller for mean ionic activity coefficients compared to activity coefficients of individual ions.
Modeling the Activity Coefficients of Individual Ions in Aqueous Solutions

a. activity coefficients of cation [312]

b. activity coefficients of anion [327]
Figure 5.7 II+IW (EDH+Born) performance of activity coefficients for electrolyte solution of Na₂SO₄.

c. mean ionic activity coefficients [30]

Figure 5.7 II+IW (EDH+Born) performance of activity coefficients for electrolyte solution of Na₂SO₄.

a. activity coefficients of cation [312]

Modeling the Activity Coefficients of Individual Ions in Aqueous Solutions
b. activity coefficients of anion [312]

c. mean ionic activity coefficients [30]

Figure 5.8 Model performance of activity coefficients for electrolyte solution of K$_2$SO$_4$.

Finally, from Figure 5.9, it can be seen that the II-IW theory performance is good for the individual ionic activities in aqueous
LaCl₃ solutions. The II and IW contributions of La³⁺ vary in a wider range than those of Cl⁻ due to their charge ratio, but still the performance is very good. We see a slightly different qualitative trend for e-CPA II+IW contributions, but still the performance of all models is acceptable and for both the single ion and mean ionic activity coefficients.

From Table 5.4 and Figures 5.1-5.9, it can be seen that all the three models can predict for many systems very satisfactorily the trend of activity coefficients of individual ions and mean ionic activity coefficients. The Born contributions from e-CPA and the Born equation are the same.

![Graph showing activity coefficients of cation](328)
b. activity coefficients of anion [328]

c. mean ionic activity coefficients [328]

Figure 5.9 Model performance of activity coefficients for electrolyte solution of LaCl$_3$. 
In all cases, the total (single ion and mean ionic) activity coefficient comes out as a balance between two opposing terms of equal magnitude, a positive contribution from the Born theory and a negative from EDH or MSA. It appears, thus, that both terms (II and IW) are of equal importance in the representation of electrolyte solutions. This conclusion is in agreement with the studies by Boda, Valiskó and Shilov.

It can be seen from Table 5.4 that for activity coefficients of anion, the best performance for all salts is from e-CPA. And for mean ionic activity coefficients, the best performance for all salts comes from MSA+Born. From the results of EDH+Born, the deviations for 2:1 electrolytes, 1:2 electrolytes, and 3:1 electrolytes, are mainly from the multivalent ions. This may be due to the limitation of Born equation for multivalent ions. Still, overall, the differences between the various modeling approaches are rather small.

As mentioned above, in MSA and EDH, the average radius is used instead of individual radii for cation and anion. In MSA and DH (e-CPA), the screening length is related to the static permittivity which is molality-dependent. In EDH, the screening length is related to the static permittivity of solvent (with no salt). These differences may be the main reasons of the different performance of different models.

For one salt, when using MSA and EDH, the II contributions of cation and anion are close for 1:1 electrolytes. This is mainly because the distance of closest approach was assumed to be the sum of the radii. This may be one of reasons that cause the deviations.

### 5.3.2 Results using e-CPA

In e-CPA, the $\Delta F$ is defined as the difference of ‘Helmholtz energy divide $RT$’ between aqueous electrolyte solution and reference state (pure solvent as the reference):

$$
\Delta F = \left( \frac{A}{RT} \right)_{V,T,n} - \left( \frac{A}{RT} \right)_{V_0,T_0,n_0}
$$

(5.18)
And the expression for the contribution terms to activity coefficient of ion is given from the equation:

\[
\ln \gamma_i = \left( \frac{\partial \Delta F^{SRK}}{\partial n_i} \right)_{V,T,n_j} + \left( \frac{\partial \Delta F^{Association}}{\partial n_i} \right)_{V,T,n_j} \\
+ \left( \frac{\partial \Delta F^{DH}}{\partial n_i} \right)_{\varepsilon_r,V,T,n_j} + \left( \frac{\partial \Delta F^{Born}}{\partial n_i} \right)_{\varepsilon_r,V,T,n_j} \\
+ \left( \frac{\partial \Delta F^{Born}}{\partial \varepsilon_r} \right)_{V,T,n_j} \left( \frac{\partial \varepsilon_r}{\partial n_i} \right)_{V,T,n_j} \\
+ \left( \frac{\partial \Delta F^{Born}}{\partial \varepsilon_r} \right)_{V,T,n_j} \left( \frac{\partial \varepsilon_r}{\partial n_i} \right)_{V,T,n_j} - \ln \frac{Z}{Z_0}
\]

In Eq. (5.19), \( \varepsilon_r \) is the relative static permittivity of solvent in electrolyte solutions, \( n_i \) is the mole number of ion \( i \), \( Z \) is the compressibility factor of solution, \( Z_0 \) is the compressibility factor of pure solvent. \( \Delta F^{SRK} \) is the \( \Delta F \) from SRK contribution, the ions have volume which cannot be ignored, and the volume-exclusion from ions is present, so, the SRK contribution is set for this. The term \( -\ln \frac{Z}{Z_0} \) is a correlation of the compressibility factor, for the difference that based on mole numbers of ions and the one based on mole number of salts. Here, in our analysis we have combined \( \left( \frac{\partial \Delta F^{SRK}}{\partial n_i} \right)_{V,T,n_j} \) and \( -\ln \frac{Z}{Z_0} \) as ‘SRK+lnZ’ contribution.

There is no association contribution for ions, but the association of solvent is affected by the presence of ions, so, the contribution from solvent association is also considered. \( \Delta F^{Association} \) is the \( \Delta F \) from the influence of solvent. We name \( \left( \frac{\partial \Delta F^{Association}}{\partial n_i} \right)_{V,T,n_j} \) as ‘Association’ contribution.
ΔF<sup>DH</sup> is the ΔF from ion-ion interaction, we name \( \frac{\partial \Delta F^{DH}}{\partial n_i} \) \(_{\epsilon_r,V,T,n_j}\) as ‘DH’ contribution. ΔF<sup>Born</sup> is the ΔF from ion solvation, we name \( \frac{\partial \Delta F^{Born}}{\partial \epsilon_r} \) \(_{V,T,n_j}\) as ‘Born’ contribution.

It needs to be pointed that the relative static permittivity is composition dependence. When obtaining the chemical potential of ions by differential computing the residual Helmholtz energy, the differential of relative static permittivity should be taken account into. We combined \( \frac{\partial \Delta F^{DH}}{\partial \epsilon_r} \) \(_{V,T,n_j}\) \( \frac{\partial \epsilon_r}{\partial n_i} \) \(_{V,T,n_j}\) and

\[ \frac{\partial \Delta F^{Born}}{\partial \epsilon_r} \] \(_{V,T,n_j}\) \( \frac{\partial \epsilon_r}{\partial n_i} \) \(_{V,T,n_j}\) as ‘Permittivity’ contribution.

So, the contributions of excess chemical potential for ion are divided into 5 parts, as summarized in Table 5.5.

### Table 5.5 Contributions of activity coefficients in e-CPA.

<table>
<thead>
<tr>
<th>No</th>
<th>Term</th>
<th>Contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \frac{\partial \Delta F^{SRK}}{\partial n_i} ) (_{V,T,n_j}) (- \ln \frac{Z}{Z_0})</td>
<td>SRK+lnZ</td>
</tr>
<tr>
<td>2</td>
<td>( \frac{\partial \Delta F^{Association}}{\partial n_i} ) (_{V,T,n_j})</td>
<td>Association</td>
</tr>
<tr>
<td>3</td>
<td>( \frac{\partial \Delta F^{DH}}{\partial n_i} ) (_{\epsilon_r,V,T,n_j})</td>
<td>DH</td>
</tr>
<tr>
<td>4</td>
<td>( \frac{\partial \Delta F^{Born}}{\partial n_i} ) (_{\epsilon_r,V,T,n_j})</td>
<td>Born</td>
</tr>
<tr>
<td>5</td>
<td>( \frac{\partial \Delta F^{DH}}{\partial \epsilon_r} ) (<em>{V,T,n_j}) ( \frac{\partial \epsilon_r}{\partial n_i} ) (</em>{V,T,n_j}) + ( \frac{\partial \Delta F^{Born}}{\partial \epsilon_r} ) (<em>{V,T,n_j}) ( \frac{\partial \epsilon_r}{\partial n_i} ) (</em>{V,T,n_j})</td>
<td>Permittivity</td>
</tr>
</tbody>
</table>

In this part, the individual ionic (and mean ionic) activity coefficients are calculated using e-CPA with the parameters from our previous...
There are no e-CPA parameters for the LaCl$_3$$+$$\text{H}_2\text{O}$ system, so this system is not considered. We present in Figures 5.10-5.17 both the complete results for e-CPA and an analysis of the individual terms. Besides the differences in the II term expression, we should point out that the calculations of II and IW terms in e-CPA are different from Valiskó and Boda’s work [44], as due to the way the dielectric constant is estimated in e-CPA, the kinetic depolarization effect is eliminated [24]. In e-CPA, the individual ion radius (from Marcus) are used instead of the average Pauling radius, and in the original e-CPA, the Born radii are different from those in Valiskó and Boda’s work. For the II calculation in e-CPA, the ion radii from Marcus are used, while Pauling radii [57] are used in II+IW calculations.

![Graph showing activity coefficients of cation](image-url)
b. activity coefficients of anion [314]

c. mean ionic activity coefficients [314]

Figure 5.10 e-CPA performance of activity coefficients for electrolyte solution of NaCl.
Modeling the Activity Coefficients of Individual Ions in Aqueous Solutions

a. activity coefficients of cation [314]

b. activity coefficients of anion [314]
c. mean ionic activity coefficients [314]

Figure 5.11 e-CPA performance of activity coefficients for electrolyte solution of NaBr.

a. activity coefficients of cation [312]
Modeling the Activity Coefficients of Individual Ions in Aqueous Solutions

b. activity coefficients of anion [312]

c. mean ionic activity coefficients [325]

Figure 5.12 e-CPA performance of activity coefficients for electrolyte solution of NaF.
Modeling the Activity Coefficients of Individual Ions in Aqueous Solutions

a. activity coefficients of cation [314]

b. activity coefficients of anion [314]
c. mean ionic activity coefficients [314]

Figure 5.13 e-CPA performance of activity coefficients for electrolyte solution of KCl.

a. activity coefficients of cation [326]
b. activity coefficients of anion [312]

c. mean ionic activity coefficients [61]

Figure 5.14 e-CPA performance of activity coefficients for electrolyte solution of CaCl$_2$. 
Modeling the Activity Coefficients of Individual Ions in Aqueous Solutions

a. activity coefficients of cation [312]

b. activity coefficients of anion [312]
c. mean ionic activity coefficients [62]

Figure 5.15 e-CPA performance of activity coefficients for electrolyte solution of MgCl₂.

a. activity coefficients of cation [312]
b. activity coefficients of anion [327]

c. mean ionic activity coefficients [30]

Figure 5.16 e-CPA performance of activity coefficients for electrolyte solution of Na₂SO₄.
Modeling the Activity Coefficients of Individual Ions in Aqueous Solutions

a. activity coefficients of cation [312]

b. activity coefficients of anion [312]
c. mean ionic activity coefficients [30]

Figure 5.17 e-CPA performance of activity coefficients for electrolyte solution of K$_2$SO$_4$.

Because the e-CPA adjustable parameters are obtained by fitting the mean ionic activity coefficients, the e-CPA model can give good agreement for the mean ionic activity coefficients. From Figures 5.10-5.17, it can be seen that, the present version of e-CPA with the parameters optimized from mean ionic activity coefficients cannot provide accurate values for the activity coefficients of individual ions. What we observe is that there is an error for both activity coefficients of cation (systematic underestimation) and activity coefficients of anion (systematic overestimation). The two effects cancel out when the activity coefficients of cation and anion are combined to yield the mean ionic activity coefficients, but the problem remains for activity coefficients of individual ions. The DH and Born effects are still large and opposing, as we have seen in the previous section, but the values are different compared to those from the II+IW theory. For most cases, the 'SRK+lnZ' term is
important, and affects the results significantly. Though the contributions from static permittivity are small, this contribution cannot be ignored. Finally, the association contribution is also of importance, especially at higher molalities (also the case for the SRK-term). The physical (SRK) and association terms have often (but not always) opposing trends (SRK negative and association positive), again especially pronounced at higher concentrations.
Still the results are not identical for all salts. While we see significant problems, as discussed above, for NaCl and NaBr as well as for CaCl$_2$, Na$_2$SO$_4$ and MgCl$_2$, the results for NaF and KCl are overall fine (and perfect for the anion coefficients). Even for K$_2$SO$_4$ (despite seeing again the under/over estimation of, respectively, the activity coefficients of cation and anion), the overall performance of e-CPA is satisfactory for both the single and mean ionic activity coefficients.
The solvent relative static permittivity of electrolyte solutions is critical for calculations of electrostatic interactions. In the original e-CPA, the relative static permittivity is calculated from a new model which eliminates the kinetic depolarization (the values are bigger than the experimental values). In the II+IW theory calculations, the relative static permittivity is calculated from the correlation equations of experimental data.
The performance for activity coefficients of individual ions is different for the II+IW theory compared to the original e-CPA. One of the main factors is the values of relative static permittivity. The importance of kinetic depolarization is always a debatable topic, and the elimination of kinetic depolarization needs more discussion. Another reason for the differences is the inclusion in e-CPA of the “physical” terms from SRK and the association contribution.

5.4 Discussion

Some further reflections on the various models’ characteristics and possible connection to their performance follow in this section. The DH-SiS model [313] neglects the non-electrostatic effects,
such as the core potential. Fraenkel [313] stated that only the size of the ion and the closest distance of the ion to its counterion are necessary individual factors in evaluating the single-ion activity. They stated that there is no need to consider ion solvation, ion pairing, and core effects in computing single-ion activities. For each activity-concentration curve, the Poisson-Fermi model [317] requires three unchanged parameters, which are associated with the Born radius.

In the II+IW model, the activities of individual ions are a result from the competing effects of the II and IW interactions. Pauling radii and Born radii should be used in II and IW calculation respectively, and molality-dependent static permittivity should be used in calculations. The II+IW model does not contain any adjustable parameter, and as all the parameters used in the model are taken from experiments, the results can be considered to be entirely predictive.

In the EDH and MSA models, the same ion radius is used for activity coefficients of cation and anion. In the II term of e-CPA, the cation radius and anion radius are used for activity coefficients of cation and anion respectively. But this difference is not reflected in the results.

Compared with the II+IW theory, CPA (SRK+Association) contribution is the extra contribution in e-CPA.

Finally, the Born equation provides a simple analytical formula for molecular electrostatic energy in the presence of implicit solvent [329]. The accuracy depends a lot on the accuracy of the so-called effective Born radii. The usual assumption that a given ion has the same size in any compound is partially true [330].

5.5 Conclusion

This chapter presents a modeling study of individual ion activities in aqueous solutions by using the II+IW theory in various forms and the e-CPA EOS. Although the II+IW models are simplified and the performance is not perfect, they can represent the basic
interactions present in electrolyte solutions. In many cases the results are in good agreement with experimental data. The ion radius, Born radius, static permittivity and other parameters are critical in the calculations with the II+IW models and e-CPA. More theoretical investigations are needed for the study of individual ion activities. For investigating the application of single ion activity coefficients in the EOS model development, fitting the model parameters to the activity coefficients of individual ions may need to be studied first.
Chapter 6. Conclusion and Future Work

6.1 Conclusion

This work presents thermodynamic modeling studies for several electrolyte solution systems with e-CPA, as well as an analysis of the model including modeling of activity coefficients of individual ions in aqueous solutions using not only e-CPA but also other electrolyte models. This work is divided into three main parts: modeling of aqueous electrolyte solutions; modeling of gas solubility in aqueous electrolyte solutions; electrolyte investigation of activity coefficients of individual ions and analysis of the terms of the electrostatic models.

In the first part, the size of quaternary ammonium cations and the respective ion-water binary interaction parameters are obtained by fitting the mean ionic activity coefficients and osmotic coefficients of aqueous solutions. Several properties of these aqueous solutions have been then studied using e-CPA with the obtained parameters.

Various modeling approaches and methods to estimate the adjustable parameters have been considered in order to investigate the effect of the number and type of adjustable parameters used. Several multi-salt solutions have been molded using e-CPA with no new adjustable parameters (thus, these results are predictions).

From the results, it can be seen that e-CPA can predict quite well mean ionic activity coefficients and osmotic coefficients of aqueous solutions of quaternary ammonium salts (QAS) and multi-inorganic salts. We also conclude that the ion size is important for electrostatic interactions, and also that the ion-pairs and hydrophobic effects play important roles on the static permittivity of aqueous solutions of QAS.

Following the modeling of aqueous solutions, gas solubility of
several gases has been studied. The ion (metal halide salts)-gas (CO$_2$, N$_2$, CH$_4$ and C$_2$H$_6$) interaction parameters are obtained by fitting the solubilities in aqueous solutions of single-inorganic salt systems. The gas solubility in aqueous solutions of multi-salt systems are then predicted using the single cation/anion-gas parameters. The ion (QAS)-gas (CO$_2$, N$_2$, CH$_4$ and C$_2$H$_6$) interaction parameters are obtained by fitting the solubilities in aqueous solutions of single-QAS. The salting effects were also extensively discussed.

e-CPA gives excellent agreement with experimental gas solubility data over wide ranges of temperature, pressure and salt molality. The e-CPA performance is reasonable for the salting effects as function of temperature and pressure as well for different ion sizes, charge densities and salt concentrations.

At the last part of this work, the activity coefficients of individual ions are investigated using various electrolyte theories. The single ionic activity of several salts has been calculated using various electrolyte models (EDH+Born, MSA+Born, II+IW in e-CPA and e-CPA). The discussion of the results and analysis of the models illustrate that several parameters like the ion radius, Born radius and dielectric constant have a significant effect on the results. Several approaches can describe well the activity coefficients of individual ions, but further investigations are required. The DH/MSA and Born terms are of equal importance for electrolyte model studies (in the sense that they are of almost similar magnitude).

### 6.2 Future Work

The thermodynamic modeling of QAS systems is challenging, because QAS exhibit hydrophobic-like character due to the alkyl chains and the low charges of cations. This hydrophobicity causes an unusual solution behavior. Adding dissociation equilibrium to the model is a potential solution for organic salt solutions where ion association and hydrophobic effects exist.
Conclusion and Future Work

The dissolution of CO₂ in H₂O contains an additional equilibrium of two acids. Introducing chemical reaction equilibria is a potential solution for improving the model performance. The next step for hydrate-related systems is the modeling of the hydrate-vapor-liquid phase equilibrium by adding a hydrate model (e.g. Van der Waals-Platteeuw model).

More experimental studies of activity coefficients of individual ions are needed for further investigation of this important effect, especially for multivalent ions and high salt concentrations. On the other hand, more in-depth studies are needed for the classical theories for electrolyte solutions e.g. about the importance of the Born contribution, the role and importance of parameters in the DH or MSA terms, as well as an analysis of the balance between electrostatic (ion-ion; ion-water) effects and the “physical” (including association) contributions of a complete electrolyte equation of state.
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Appendix

A. PhD Activities

A.1 List of Publications
Publications as first author, in international peer-reviewed journals:

A.2 Contributions at Conferences
A.2.1 International Conferences
Li Sun, Xiaodong Liang, Nicolas von Solms, and Georgios M. Kontogeorgis
Modeling Tetra-n-butyl Ammonium Halides Aqueous Solutions with the e-CPA Equation of State (Oral)
The 30th European Symposium on Applied Thermodynamics
Prague, Czech Republic, June 10-13 2018

Li Sun, Xiaodong Liang, Nicolas von Solms, and Georgios M. Kontogeorgis
Modeling of Gas Solubility using the e-CPA Equation of State (Oral)
The 36th International Conference on Solution Chemistry
Xining, China, August 4-8 2019
A.2.2 Internal Conferences
Li Sun, Xiaodong Liang, Nicolas von Solms, and Georgios M. Kontogeorgis

*Modeling of Gas Solubility in Aqueous Electrolyte Solutions using the e-CPA Equation of State (Oral)*
CERE Annual Discussion Meeting
Helsingør, Denmark, June 11-13 2019

Li Sun, Xiaodong Liang, Nicolas von Solms, and Georgios M. Kontogeorgis

*Modeling of Gas Solubility in Aqueous Electrolyte Solutions using the e-CPA Equation of State (Poster)*
CERE Annual Discussion Meeting
Helsingør, Denmark, June 11-13 2019

Li Sun, Xiaodong Liang, Nicolas von Solms, and Georgios M. Kontogeorgis

*Thermodynamic Study on Ionic Liquid-Water as Alternative Working Pairs for Absorption Refrigeration Cycle (Poster)*
CERE Annual Discussion Meeting
Helsingør, Denmark, June 11-13 2019

Li Sun, Xiaodong Liang, Nicolas von Solms, and Georgios M. Kontogeorgis

*Modeling Tetra-n-butyl Ammonium Halides Aqueous Solutions with the Electrolyte CPA Equation of State (Poster)*
CERE Annual Discussion Meeting
Helsingør, Denmark, June 21-23 2018

Li Sun, Xiaodong Liang, Nicolas von Solms, and Georgios M. Kontogeorgis

*Modeling Tetra-n-butyl Ammonium Halides Aqueous Solutions with the Electrolyte CPA Equation of State (Oral)*
CERE Annual Discussion Meeting
Helsingør, Denmark, June 21-23 2018
Li Sun, Xiaodong Liang, Nicolas von Solms, and Georgios M. Kontogeorgis
*Modeling CO2 semi-clathrate hydrate related systems: literature review and database (Poster)*
KT Consortium Annual Meeting
Helsingør, Denmark, June 6-8 2017

Li Sun, Xiaodong Liang, Nicolas von Solms, and Georgios M. Kontogeorgis
*Modeling CO2 semi-clathrate hydrate related systems: literature review and database (Oral)*
CERE Annual Discussion Meeting
Snekkersten, Denmark, June 21-23 2017

A.3 Attended Courses
28930 Advances in Chemical and Biochemical Engineering, 2019
28928 Electrolyte Solution Thermodynamics, 2018
28917 Statistical Thermodynamics for Chemical Engineering, 2018
28909 Thermodynamic Models, Fundamentals and Computational Aspects, 2017
28901 Advanced Computer Aided Modelling, 2017

A.4 Teaching
Teaching assistant in 28221 Chemical Engineering Thermodynamics (2018)
Teaching assistant in 28221 Chemical Engineering Thermodynamics (2019)
Teaching assistant in 28322 Chemical Engineering Thermodynamics (2019)
B. Experimental Analysis of Activity Coefficients of Individual Ions

Table B.1 Summary of experimental studies for activity coefficients of individual ions.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Cation</th>
<th>Anion</th>
<th>Molality</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
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<td>-</td>
<td>X</td>
<td>0.003-2.0</td>
<td>[312]</td>
</tr>
<tr>
<td></td>
<td>X</td>
<td>X</td>
<td>0.0005-0.506</td>
<td>[331]</td>
</tr>
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<td>X</td>
<td>0.1-4.0</td>
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</tr>
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<td>X</td>
<td>X</td>
<td>0.001-3.0</td>
<td>[326]</td>
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<td></td>
<td>X</td>
<td>X</td>
<td>0.01632-1.091</td>
<td>[332]</td>
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<td>Activity Coefficient Range</td>
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<tr>
<td>LaCl₃</td>
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</table>

a. only activity coefficients of anion are measured;
b. only activity coefficients of cation are measured.
Table B.2. A summary of experimental data used in modeling.

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<th>-</th>
<th>±</th>
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<tr>
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</tr>
</tbody>
</table>

(a) NaCl

Red Symbols: Mean ionic Lit.  Green Symbols: Calculated from Single ion
(b) KCl

(c) CaCl2
Appendix

(d) MgCl_2

(e) NaBr
(f) NaF

(g) Na₂SO₄
Figure B.1. Comparison of mean ionic activity coefficients between calculated values from activity coefficients of individual ions and direct experimental values.
Figure B.2. Activity coefficients of individual ions in different aqueous electrolyte solutions.