Modelling of Ion Activity Coefficients:
Extended Specific Ion Theory With Ion Pairing

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ABSTRACT

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The ratio of a substance's chemical activity to its molar concentration is known as the activity coefficient in chemistry. The activity coefficient, which is 1 in an ideal solution where each molecule's efficiency is equal to its theoretical effectiveness, is a measure of how much a solution deviates from the ideal state.

Some properties of ions in solution are very non-ideal. Even at a low concentration, the activity coefficient is different from one. In basic chemistry, it is common to use concentration or molality instead of activity to calculate equilibria. As long as concentration is small, the activity coefficient is assumed to be one. However, for ions, it can be observed that even at very low concentration, e.g., 0.01 mol/L or mol/kg the activity coefficient is already very different from one (e.g., 0.903 for NaCl). That is why it is important to calculate activity coefficients for chemical equilibrium calculations with ions. Examples of applications are like hydrometallurgy, solubility of metal compounds, scaling, and any crystallisation process of electrolytes. In these cases, it is important to predict the equilibrium and so activity coefficient prediction is needed.

The Specific Ion Theory (SIT) model and Pitzer model are the most popular models to predict activity coefficients of ions in solutions. However, neither of these models account for ion pairing. Ion paring is the formation of dissolved molecules from the ions (e.g., $MgSO_4$(aq)). The purpose of this thesis is to build a model that accounts for ion pairing and predict activity coefficient. The SIT model was used as a basis. The model successfully predicted the activity coefficients of most 1-1 and 2-2 electrolytes to about 1 % accuracy. Including ion pairing improved the accuracy of the SIT model, particularly in the case of 2-2 electrolytes (from about 10 % to about 1 %).

ACKNOWLEDGEMENTS

DEDICATION

To Amir Pouya

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Symbol	Definition
ε_{cX}	Interaction parameter between cation c and anion X
$A^-(\text{aq})$	Anion in aqueous solution
$C^+(\text{aq})$	Cation in aqueous solution
e^-	Electron
f^γ	Debye-Huckel term (Pitzer model)
G^E	Excess Gibbs free energy
k_B	Boltzmann constant
N_A	Avogadro's constant
W_w	Water mass in kg
z_i	Charge number of i
$\gamma_\pm$	Mean activity coefficient
γ_M	Activity coefficient of cation M
γ_X	Activity coefficient of anion X
ε_0	Permittivity of vacuum
ε_r	Relative permittivity of water
λ_{ij}	Binary interaction parameter
μ_{ijk}	Interaction parameter of species i, j, and k
$\psi_{CAA'}$	Ternary interaction parameters between a cation and two anions
$\psi_{CC'A}$	Ternary interaction parameters between two cations and an anion

Φ_{Aa}	Binary interaction parameter between two anions
Φ_{Cc}	Binary interaction parameter between two cations
A	Debye-Huckel constant (0.51 at 25 °C)
a	Ion diameter in Debye-Huckel extended law
B	Parameter in Debye-Huckel extended law
b	Pitzer parameter for the Debye-Huckel term
c	Cation
CA	Electrolyte with cation C and anion A
CA(aq)	Refers to the ion pair of cation C and anion A
CA^0	Refers to the ion pair of cation C and anion A
EMF	Electromotive force
I	Ionic strength
m	Molality
$m_{A,app}$	Apparent molality of A
m_c	Molality of cation c
$m_{C,app}$	Apparent molality of ion C
M_cX_a	Electrolyte with c cations M and a anions X
m_i	Molality of compound i
pH	Measure of acidity/basicity
R	Universal gas constant (8.314 j/mol)
SIT	Specific Ion Theory
T	Temperature

x	Variable of function g in Pitzer model
Z	Charge number
α	Coefficient in Pitzer model
β	Pitzer parameter
ρ_w	Density of water
θ	Pitzer parameter

Chapter 1. Introduction

1.1 Introduction

To meet the requirements of chemical processes on an industrial scale, knowledge of physicochemical properties such as vapour pressures, boiling points, and vaporisation enthalpies of all the constituents and mixes is required (design and optimization). The thermophysical characteristics of the coexisting fluids are predicted using vapor liquid phase equilibrium (VLE) calculations, as a function of the system pressure (p) the temperature (T), and the composition (x) of the coexisting phases. These properties include the density of the coexisting fluids, heat capacity, enthalpy, and entropy. For instance, to design a distillation column for an actual distillation operation, VLE information is essential.

In some processes, the properties of ions in solutions affect relevant properties such as solvent vapor pressure, solubility of minerals, and electrolyte heat capacities. Examples of such processes are desalination, steam production (scaling), and hydrometallurgy. A key property of the ions that is needed is the activity coefficient.

This section provides a very quick overview of the ion interaction method's historical evolution. In the first two decades of last century, physical chemists were greatly perplexed by the peculiarities of strong electrolyte solutions. After several works emphasised the relevance of the long-range nature of electrostatic forces, Milner (1912) developed a theory in 1912, but its mathematical structure was challenging, and he only got approximative findings. Debye and Huckel achieved a significant simplification in the formulation of the theory in 1923 and arrived at the straightforward limiting law that answered the key conundrum. However, before Debye and Huckel, Lewis and Linhart and Bronsted had offered an extension of the limiting rule based on the interaction coefficient, and Lewis and Randall (1921) had suggested using the ionic strength as the proper electrical concentration. The ionic strength is:

$$I = \frac{1}{2}\sum_i m_i \, z_i^2 \quad \text{(1-1)}$$

Where m is the molality of the ion species i of charge z_i protonic units. Later extensions of the Debye and Huckel theory also use the ionic strength as a starting point. Details are given in Chapter 2.

Ion pairing is the association between a cation and an anion in electrolyte solution (See Chapter 3, Section 3.2). An ion pair is a species distinct from the original cation and anion. When the ion pairing is weak, the interaction is similar to nonspecific interactions, i.e., the competition between ions for water molecules. If the ion pairing is strong, there will be a different behavior. As a result, it can be expected that thermodynamic models do not need to include ion pairing when it is weak, but that ion pairing should be included when it is strong. Most thermodynamic models of electrolytes do not include ion pairing.

1.2 Objectives and structure of the thesis

One of the properties that are needed for equilibrium calculation of real solutes is the activity coefficient. In the case of ions in solution, this requires knowledge of ion interaction.

Ion interaction can occur in the form of ions affecting the behaviour of other ions. De Visscher (2018) argued that ion interaction is actually a competitive interaction between ions and water molecules. The main models used for predicting ion activity coefficients are based on equations for these kinds of interactions. However, ions can also form a chemical bond and form ion pairs. This reduces the density of net charges in the solution, and therefore reduces the ionic strength.

In most of the thermodynamic models to predict ion activity coefficients, ion pairing is not accounted for. Therefore, these models overestimate the ionic strength. The purpose of this thesis is to develop a model that is relatively simple and accurate, and that accounts for ion pairing explicitly.

In the rest of this thesis, Chapter 2 is a literature review that gives an overview of the most commonly used ion interaction models and some of their applications. Chapter 3 outlines the model developed in this work. Chapter 4 presents the data analysis of literature data on ion activity coefficients with the model developed in Chapter 3. Chapter 5 is a summary of the conclusions of the thesis.

Chapter 2. Literature Review:

2.1. Solution Chemistry

2.1.1 Electrolytes

In chemistry, an electrolyte is a dissolved substance in an aqueous solution whose electrical conductivity is higher than that of pure water. Note that the desired solute in the solution is in the form of ions. In fact, an electrolyte is partially or completely ionized in water.

As mentioned, electrolytes are chemicals that have free ions. Therefore, these materials in combination with water will lead the flow of electricity. The most common electrolytes are ionic solutions. Note that in addition to salt solutions, ions also exist in acidic and basic solutions. On the other hand, covalent dissolved chemicals are only in molecular form in the solution, so they will not increase the conductivity of the solvent. This type of chemicals is called non-electrolyte. Note that most organic substances (except organic acids or bases) are non-electrolytes, such as ethanol, methanol, sugar, glycerin, etc. Also, distilled water and solutions of non-polar compounds such as iodine in water or iodine in carbon tetrachloride are considered non-electrolytes.

Electrolytes are generally divided into two categories: strong electrolytes and weak electrolytes. Strong electrolytes are chemicals that are highly ionized. For example, strong acids and salts that exist in aqueous solutions in completely ionic form are considered as types of strong electrolytes. These materials are completely ionized in the solution and cause electric charge to be carried in the desired solution. As a result, they facilitate an electric current.

Weak Electrolytes are chemicals that are not completely ionized. For example, weak acids and bases that are not completely ionized in aqueous solutions are considered weak electrolytes. In other words, polar covalent compounds that are incompletely dissociated in aqueous solution are also included in this category.

Most atoms do not have eight electrons in their valence shell. By examining the periodic table, we realize that some atoms have only a few electrons in their last layer. When an atom has 1 or 2 electrons in its outer shell, it simply loses them to achieve a stable noble gas arrangement. Atoms that lose electrons become positively charged because they have fewer electrons to balance the positive charge of protons in the nucleus. Atoms with 6 or 7 electrons in their outer shell reach a stable arrangement by taking one or two electrons. These atoms that have lost or gained electrons are called ions. Positively charged ions are called cations. Most metals, including alkali and alkaline earth metals, as well as transition metals, are converted into cations when forming ionic compounds.

We can show the electron transfer process between sodium and chlorine atoms by using the electron arrangement. The electronic arrangement of sodium is as follows:

$$Na : 1S^2 2S^2 2P^6 3S^1$$
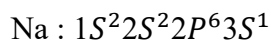
As shown above, sodium had one electron in the third shell. It loses an electron to form an octet arrangement in its last shell. Its reaction can be shown as follows:

$$Na \rightarrow Na^+ + e^-$$

Electron configuration of the cation, Na^+, is as follows:

$$Na^+ : 1S^2 2S^2 2P^6$$
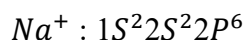
In this situation, the outermost layer of the sodium ion is its second layer, which has eight electrons. As a result, it obeys the octet rule.

The electron configuration of the chlorine atom is as follows:

$$Cl : 1S^2 2S^2 2P^6 3S^2 3P^5$$
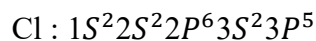
This atom needs only one more electron to increase the number of electrons in its valence shell to eight. In salt, this electron is supplied from the sodium atom.

An ionic bond is a type of chemical bond that occurs through the attraction of unlike charges in ions. According to the said material, ions are not found alone, but they form a crystal network by bonding with non-identical ions. The compound formed is called an ionic bond.

The most common type of ionic bond can be found in compounds of metals with nonmetals. Metals become stable by losing a small number of electrons. This property is known as electropositivity. On the other hand, nonmetals gain stability by gaining a few electrons. This tendency to attract electrons is called "electronegativity". When a highly electropositive metal combines with a highly electronegative nonmetal, the extra electrons are transferred from the metal atom to the nonmetal. As a result of these interactions, metal cations and non-metal anions are produced.

To understand ions in aqueous solution, it is useful to understand the properties of water. One of these properties is hydrogen bonding. Hydrogen bonding is a weak type of force that causes dipole-dipole attraction. This bond is formed when a hydrogen atom forms a bond with an atom that has a high electronegativity and at the same time is next to another electronegative atom that has a non-bonding electron pair. These types of bonds are stronger than the usual dipole-dipole and dispersion forces, but weaker than covalent and ionic bonds. Also many elements form bonds with hydrogen.

For example, consider two water molecules approaching each other. Hydrogen with charge δ^+, is strongly attracted to the non-bonding electron pair in the oxygen of the other water molecule, as if it intends to form a coordination (dative) bond. This attraction is significantly stronger than dipole-dipole interactions. The hydrogen bond strength is about ten percent of a covalent bond. These types of bonds are continuously formed and broken in liquid water.

Water is a very good example of hydrogen bonding. Note that each water molecule has the ability to form four hydrogen bonds with surrounding water molecules. In fact, the number of hydrogens δ^+, it is exactly the same as the number of lone pairs of electrons, and as a result, each can participate in hydrogen bonding.
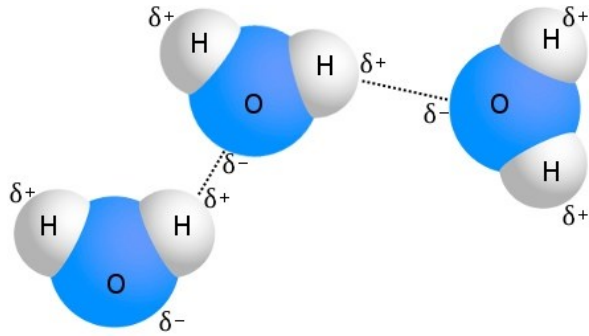
Figure 2.1. Hydrogen bonding for water (H_2O)

2.2. Models for ion activity coefficients

The literature review continues with an overview of the main activity coefficient models for electrolytes, followed by a summary of applications.

2.2.1. Debeye-Huckel limiting law

In 1923, Debeye and Huckel made the attempt to predict activity coefficients of ions based on calculating electrostatic effects (Debye and Huckel, 1923). Debeye and Huckel found the following simplified equations:

$$\log \gamma_M = -A\, Z_M^2\, \sqrt{I} \qquad \text{(2-1)}$$
$$\log \gamma_X = -A\, Z_X^2\, \sqrt{I} \qquad \text{(2-2)}$$

Where A $= \alpha/ln\,10 = 0.51$ kg$^{1/2}$ mol$^{-1/2}$ at 298 K, or more generally:

$$A = \frac{e^3 \sqrt{N_A}}{4\sqrt{2}\pi(\varepsilon_0 \varepsilon_r k_B T)^{3/2} ln10} \qquad \text{(2-3)}$$

Where N_A is the Avogadro number, ε_0 is the permittivity of free space, ε_r is the dielectric constant of water, k_B is the Boltzmann constant, and T is the temperature in K. Z_M is the charge number, I is the ionic strength which is defined as:

$$I = \frac{1}{2} \sum_{i=1}^{n} z_i^2 m_i \quad (2\text{-}4)$$

Where m_i is the molality of the ion i ($^{mol}/_{kg}$) and z_i is the charge number of ion i.

For the mean activity coefficient ($\gamma_\pm$) of an electrolyte MX, where M is the cation and X is the anion, they derived the following:

$$\log \gamma_\pm = -A \, |z_M \, z_X| \, \sqrt{I} \quad (2\text{-}5)$$

The mean activity coefficient of an electrolyte M_cX_a is defined as

$$\gamma_\pm = \sqrt[a+c]{\gamma_M^c . \gamma_M^a} \quad \text{or} \quad \log \gamma_\pm = \frac{c}{a+c} \log \gamma_M + \frac{a}{a+c} \log \gamma_X \quad (2\text{-}6)$$

The Debye-Huckel limiting law is illustrated in Figure 2.2. The figure compares the Debye-Huckel limiting law with experimental activity coefficient data for NaCl (Hamer and Wu, 1972). It is clear from the figure that the agreement between theory and experiment is only good for very low molalities (< 0.02 mol/kg).
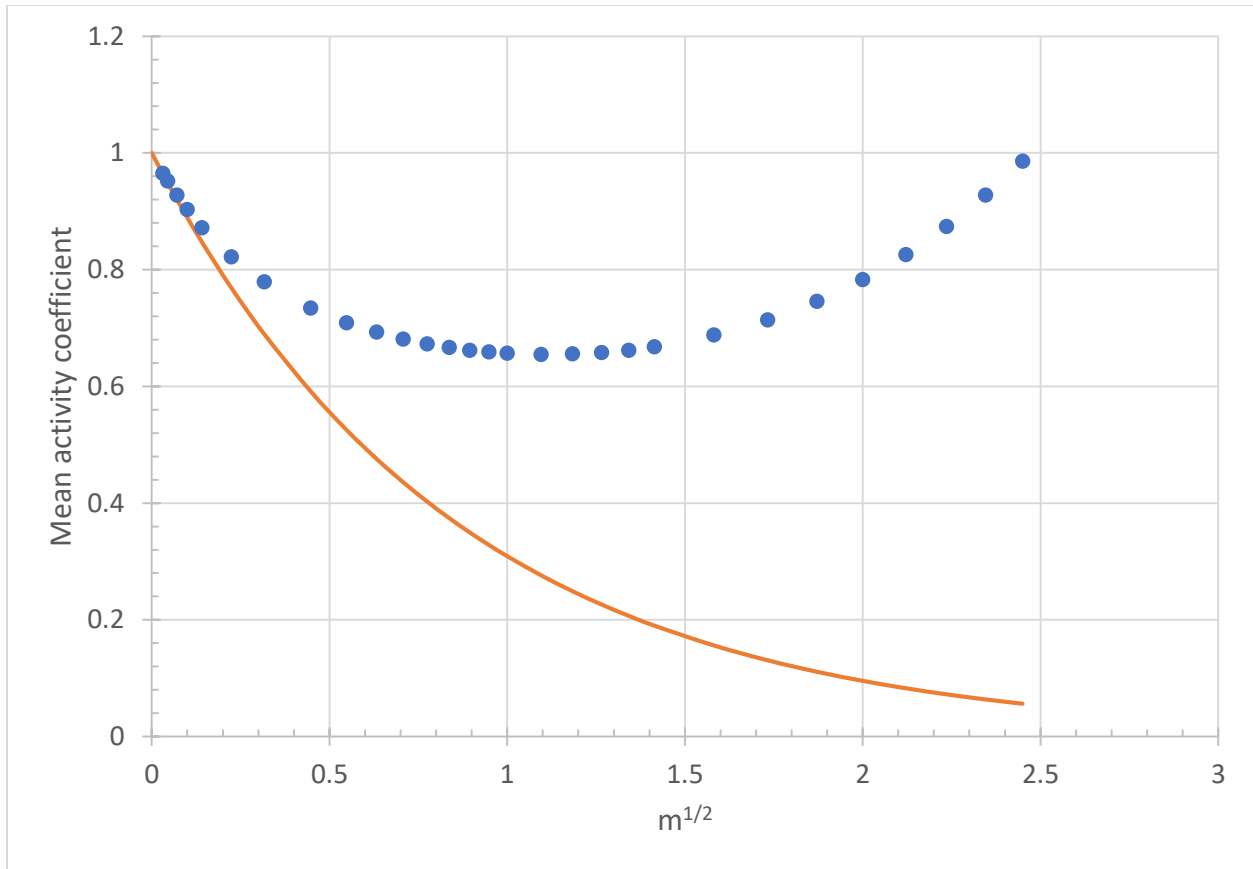
Figure 2.2. Debye-Huckel limiting law (line) and experimental activity coefficient data of NaCl (circles)

2.2.2. Extended Debye- Huckel limiting law

In 1923, Debye and Huckel also derived an extended equation, valid in a more extended concentration range (Debye and Huckel, 1923):

$$\log \gamma_M = \frac{-A\, Z_M^2\, \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} \quad (2\text{-}7)$$

Where A is the same as in Section 2.2.1. B is given by:

$$B = \left(\frac{2e^2 N_A}{\varepsilon_0 \varepsilon_r k_B T}\right)^{1/2} \quad (2\text{-}8)$$

9

Where e is the electric charge and a is the ion diameter. The agreement between the extended Debye-Huckel equation and experimental data for NaCl is shown in Figure 2.3. The addition of the denominator extends the range of the model to about 0.2 mol/kg.
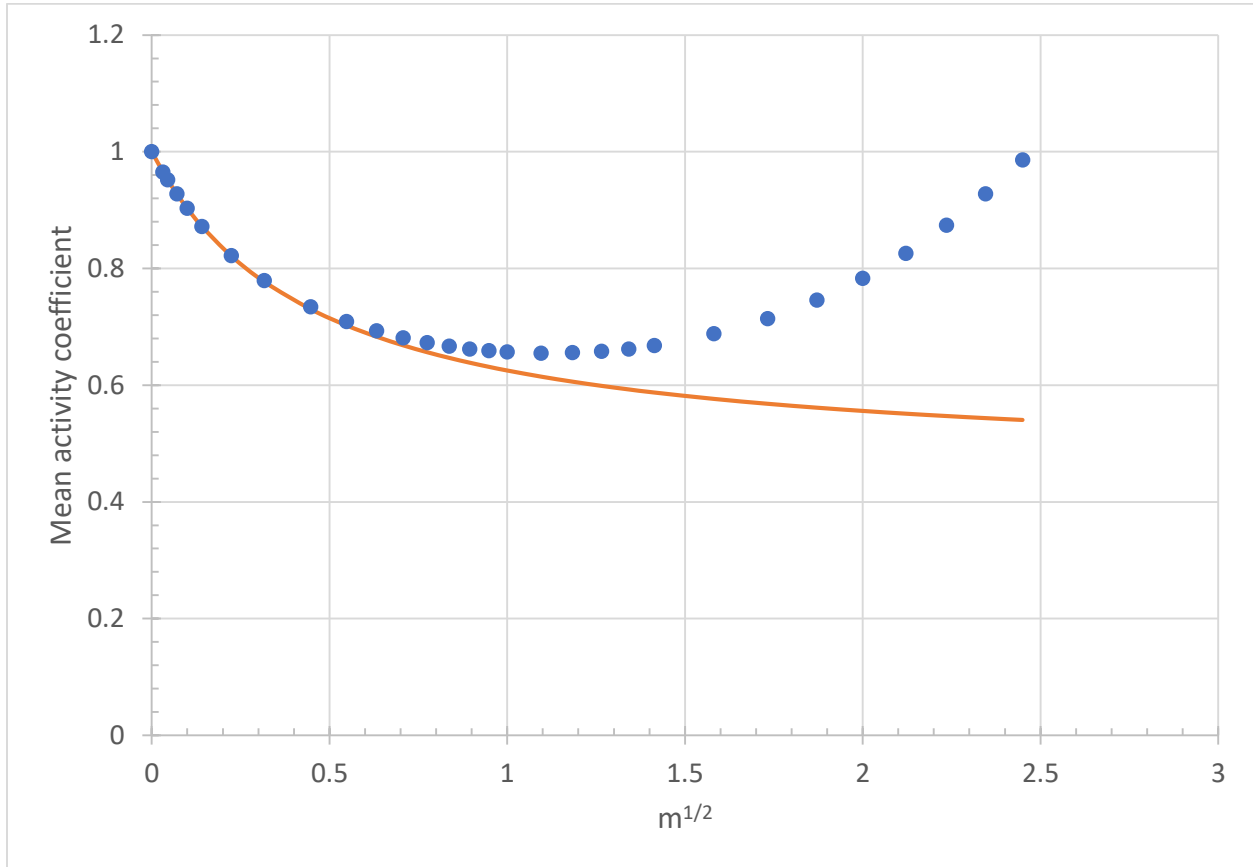
Figure 2.3. Extended Debye- Huckel model (line) and experimental activity coefficient data of NaCl (circles)

2.2.3. Davies Equation   [1938]

In 1938, Davies proposed the following equation for the activity coefficient (Davies, 1938):

$$\log \gamma_M = -A\, Z_M^2\, \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3\, I \right) \quad (2\text{-}9)$$

This equation consists of two terms: a Debye-Huckel term representing electrostatic interactions, and a term representing other interactions.

The model prediction is shown in Figure 2.4, together with reported data of NaCl. The model overestimates the activity coefficient for NaCl. This is because the value of 0.3 in the equation is an average for all electrolytes, which is clearly too high for NaCl.
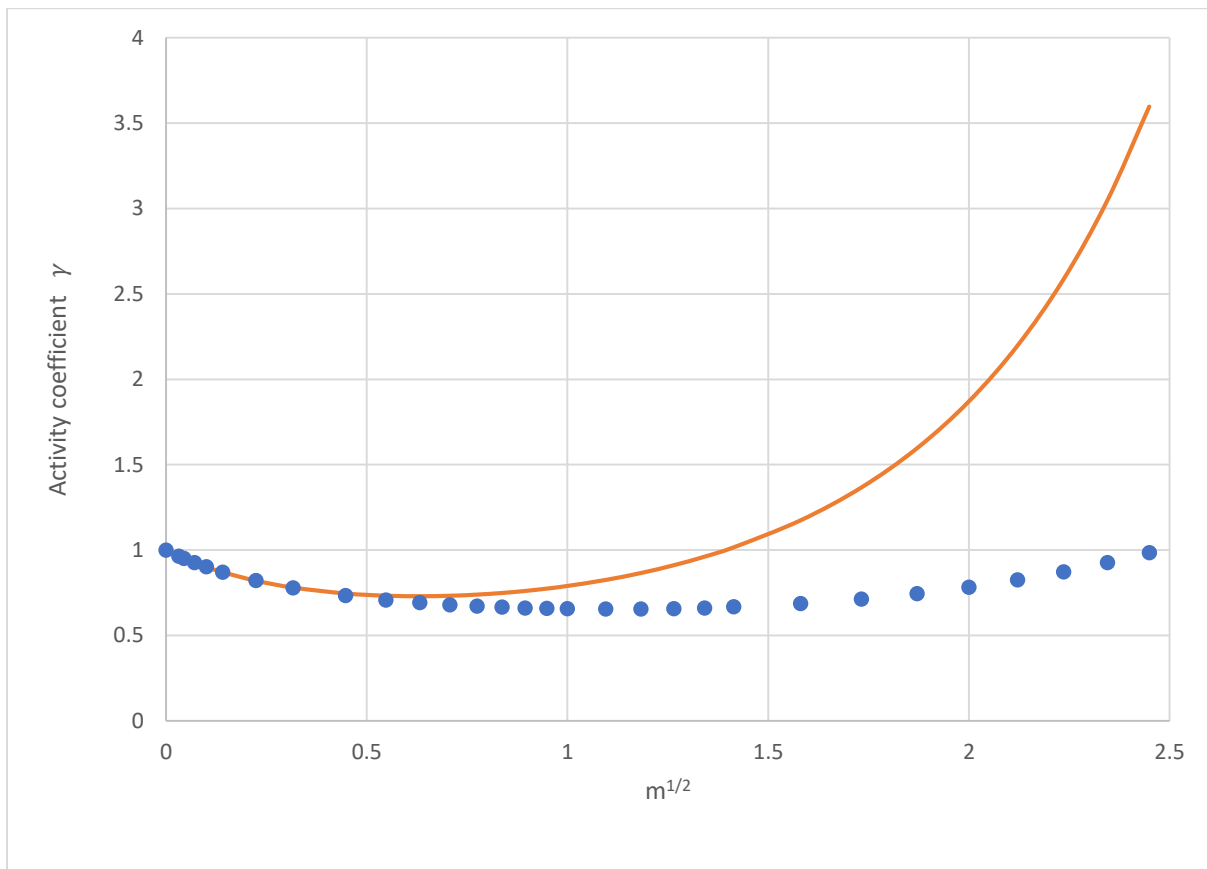
Figure 2.4. Davies (line) and experimental activity coefficient data of NaCl (circles)

2.2.4. Guggenheim Equation   [1955]

It was observed in Figure 2.4 that one coefficient in the second term does not fit all electrolytes. For that reason, Guggenheim and Turgeon (1955) proposed the following equation:

$$\log \gamma_{\pm} = -Z_M^2 \; \frac{A\sqrt{I}}{1 + \sqrt{I}} + B \cdot m \qquad (2\text{-}10)$$

It allows to use a different value of B for different electrolytes. As a result, this model gives a better agreement with the data for NaCl than the Davies equation. This is shown in Figure 2.5.
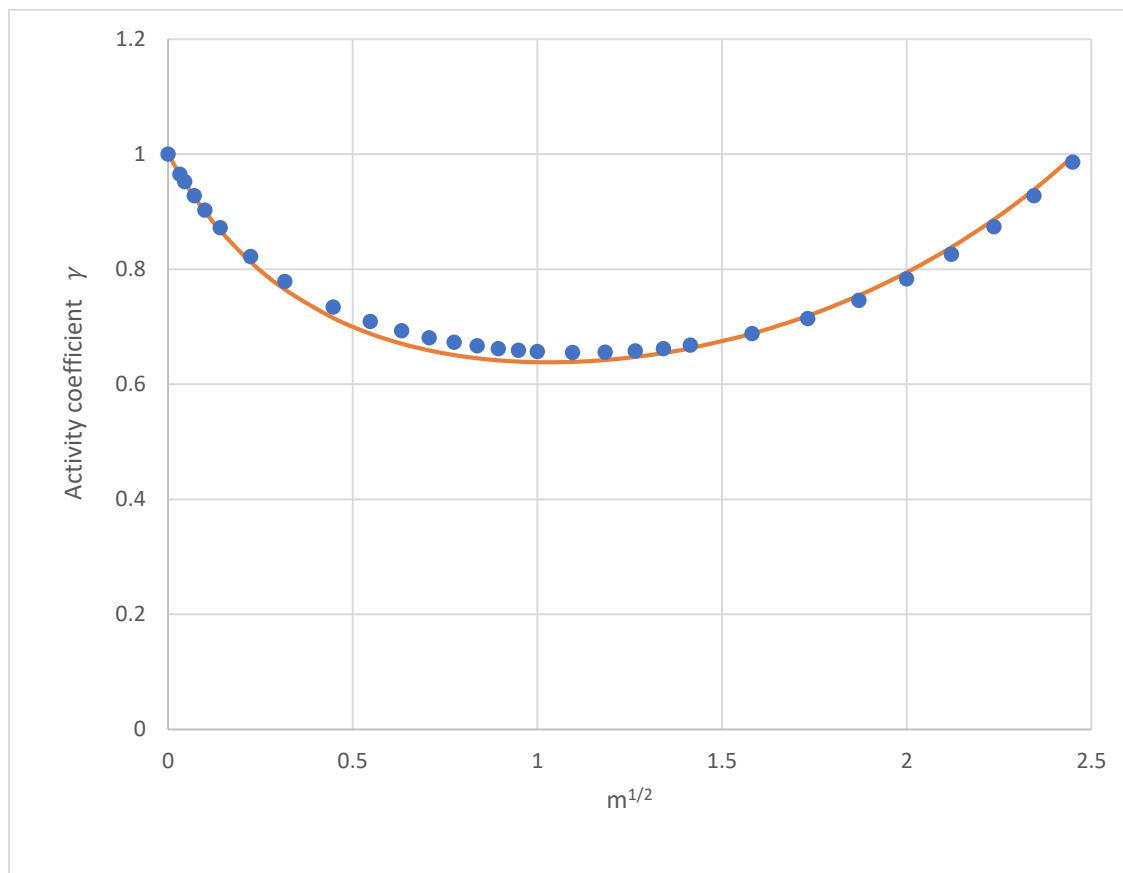
Figure 2.5. Guggenheim (line) and experimental activity coefficient data of NaCl (circles)

For NaCl, the Guggenheim equation is accurate in the entire molality range with an error of a few percent.

2.2.5. Specific Ion theory (SIT)

The Guggenheim equation formed the basis for the Specific Ion Theory (SIT) (Preis and Gamsjager, 2001):

$$\log \gamma_M = -Z_M^2 \; \frac{A\sqrt{I}}{1 + 1.5\sqrt{I}} \; + \Sigma_a \; \varepsilon_{Ma} \cdot m_a \quad (2\text{-}11)$$

$$\log \gamma_X = -Z_X^2 \; \frac{A\sqrt{I}}{1 + 1.5\sqrt{I}} \; + \Sigma_c \; \varepsilon_{cX} \cdot m_c \quad (2\text{-}12)$$

The main advantage of the specific ion theory is that it can be used for mixtures. Each ion in the mixture contributes a term to the activity coefficient.
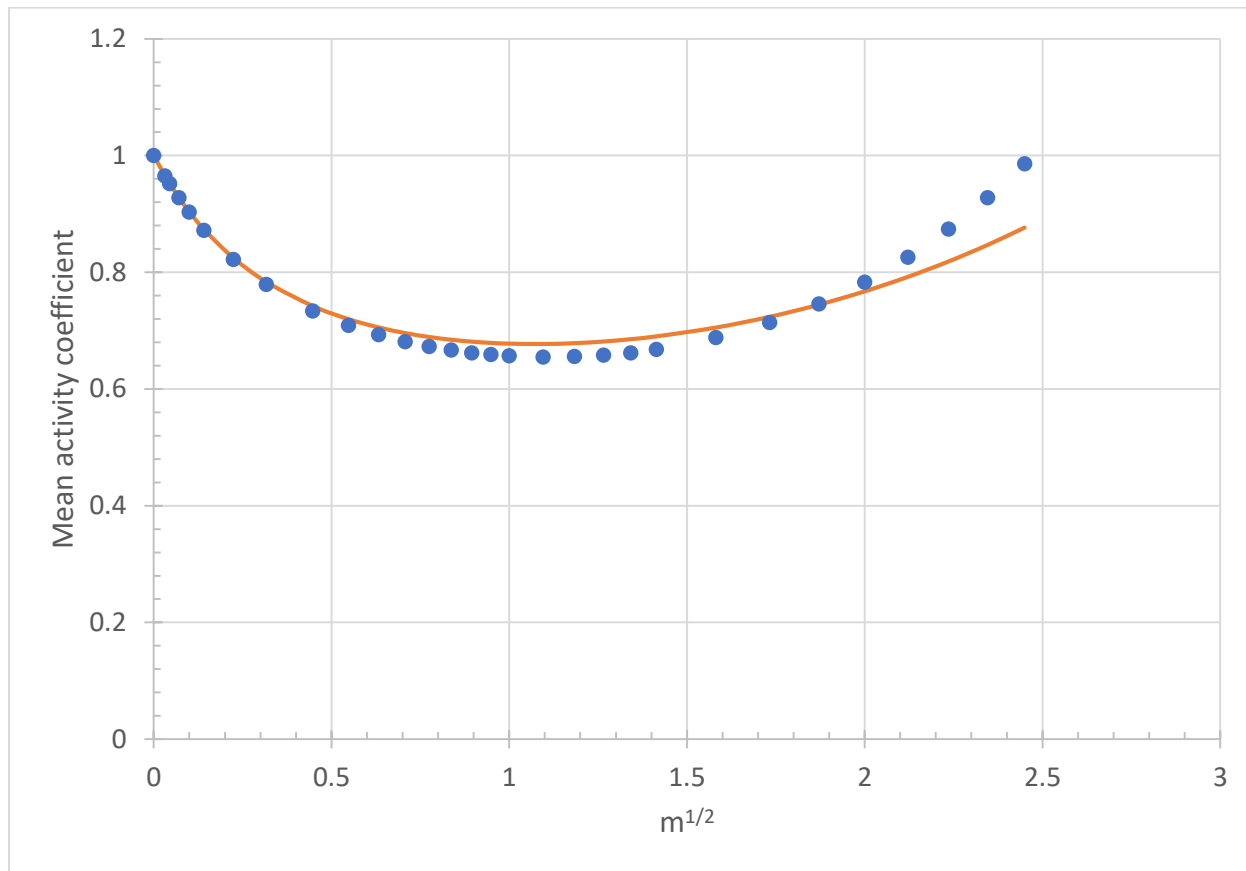
Figure 2.6. SIT model (line) and experimental activity coefficient data of NaCl (circles)

The SIT model is compared with the data for NaCl in Figure 2.6. For NaCl, the accuracy of the specific ion theory is less than the accuracy of the Guggenheim equation, particularly for molalities above 4 mol/kg. For some electrolytes, the SIT model is more accurate than the Guggenheim equation.

2.2.6. Pitzer model

Pitzer and coworkers developed a detailed model for the activity coefficients of ions in complex mixtures up to 6 mol/kg (Pitzer, 1973; Pitzer and Mayorga, 1973, 1974; Pitzer and Kim (1974). The model starts from the excess Gibbs free energy of solution:

$$\frac{G^E}{W_w RT} = f(I) + \sum_i \quad \sum_j m_i \cdot m_j \, \lambda_{ij}(I) + \sum_i \quad \sum_j \sum_k m_i \cdot m_j \cdot m_k \, \mu_{ijk} + \dots \quad (2\text{-}13)$$

Where f(I) is a function of ionic strength, and λ and μ are ion interaction parameters that have to be determined experimentally. This leads to the following equations for the activity coefficients of a cation C and an anion A:

$$\ln \gamma_C = z_C^2 F + \sum_a m_a \left(2 B_{Ca} + Z C_{Ca} \right) + \sum_c m_c \left(2 \Phi_{Cc} + \sum_a m_a \psi_{Cca} \right)$$
$$+ \sum_{a<a'} \sum_{a'} m_a m_{a'} \psi_{Caa'} + z_C \sum_c \sum_a m_c m_a C_{ca} + 2 \sum_n m_n \lambda_{nC} \qquad (2\text{-}14)$$

$$\ln \gamma_A = z_A^2 F + \sum_c m_c \left(2 B_{cA} + Z C_{cA} \right) + \sum_a m_a \left(2 \Phi_{Aa} + \sum_c m_c \psi_{cAa} \right)$$
$$+ \sum_{c<c'} \sum_{c'} m_c m_{c'} \psi_{cc'A} + z_A \sum_c \sum_a m_c m_a C_{ca} + 2 \sum_n m_n \lambda_{nA} \qquad (2\text{-}15)$$

Where B, C, Φ, λ, and ψ are ion interaction parameters, discussed below, and a and c are anions and cations other than A and C, respectively. Z is given by:

$$Z = \sum_i m_i |z_i| \quad (2\text{-}16)$$

where i refers to all ions. F is given by:

$$F = f^\gamma + \sum_c \sum_a m_c m_a B'_{ca} + \sum_{c<c'} \sum_{c'} m_c m_{c'} \Phi'_{cc'} + \sum_{a<a'} \sum_{a'} m_a m_{a'} \Phi'_{aa'} \quad (2\text{-}17)$$

In this equation, f^γ is given by:

$$f^\gamma = -A_\phi \left(\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b} \ln\left(1+b\sqrt{I}\right) \right) \quad (2\text{-}18)$$

With

$$A_\phi = \frac{1}{3} \sqrt{\frac{2\pi N_A \rho_w}{1000}} \left(\frac{e^2}{\varepsilon kT} \right)^{3/2} \quad (2\text{-}19)$$

and

$$b = 1.2. \quad (2\text{-}20)$$

f^γ is the Debye-Huckel term for the Pitzer model. At 25 °C, the parameter A_ϕ is 0.3915.

There are five types of ion interaction parameters in the model: B, C, Φ, λ, and ψ.

B_{CA} is a binary interaction parameter between cation C and anion A. It is dependent on the ionic strength as follows:

$$B_{CA} = \beta_{CA}^{(0)} + \beta_{CA}^{(1)} \cdot g\left(\alpha_1 \sqrt{I}\right) + \beta_{CA}^{(2)} \cdot g\left(\alpha_2 \sqrt{I}\right) \quad (2\text{-}21)$$

where $\beta_{CA}^{(0)}$, $\beta_{CA}^{(1)}$, and $\beta_{CA}^{(2)}$ are ion-specific constants and g is a function:

$$g(x) = 2\frac{1-(1+x)\exp(-x)}{x^2} \quad (2\text{-}22)$$

For 2-2 electrolytes, $\alpha_1 = 1.4$ and $\alpha_2 = 12$. For all other electrolytes, $\alpha_1 = 2$ and $\alpha_2 = 0$.
In the equation for F, the variable B'$_{CA}$ is the derivative of B_{CA} with respect to ionic strength.

C_{CA} is an interaction parameter that combines the interactions between two cations C and one anion A, and between one cation C and two anions A. It is independent of I.

$\Phi_{CC'}$ and $\Phi_{AA'}$ are interaction parameters between two cations C and C', and between two anions A and A', respectively. They are dependent on the ionic strength when the ions have a different charge. For instance, $\Phi_{CC'}$ is written as:

$$\Phi_{CC'} = \theta_{CC'} + {}^E\theta_{CC'}(I) \quad (2\text{-}23)$$

$\theta_{CC'}$ is independent of I. ${}^E\theta_{CC'}(I)$ is zero when the charge of C and C' is the same and a function of I if they are not the same. The function cannot be calculated analytically and must be calculated numerically. The numerical procedure will not be discussed here. Details are given by Pitzer (1991).

λ_{nC} and λ_{nA} represent the interaction between a neutral molecule n and a cation C or anion A, respectively. It is independent of ionic strength.

$\psi_{CC'A}$ and $\psi_{CAA'}$ are ternary interaction parameters between two cations and an anion, or between a cation and two anions, respectively. They are independent of ionic strength.

The parameters of the Pitzer model are determined mainly with electrochemical measurements of electrolyte mixtures with ion selective electrodes, and summarized by Pitzer (1991).
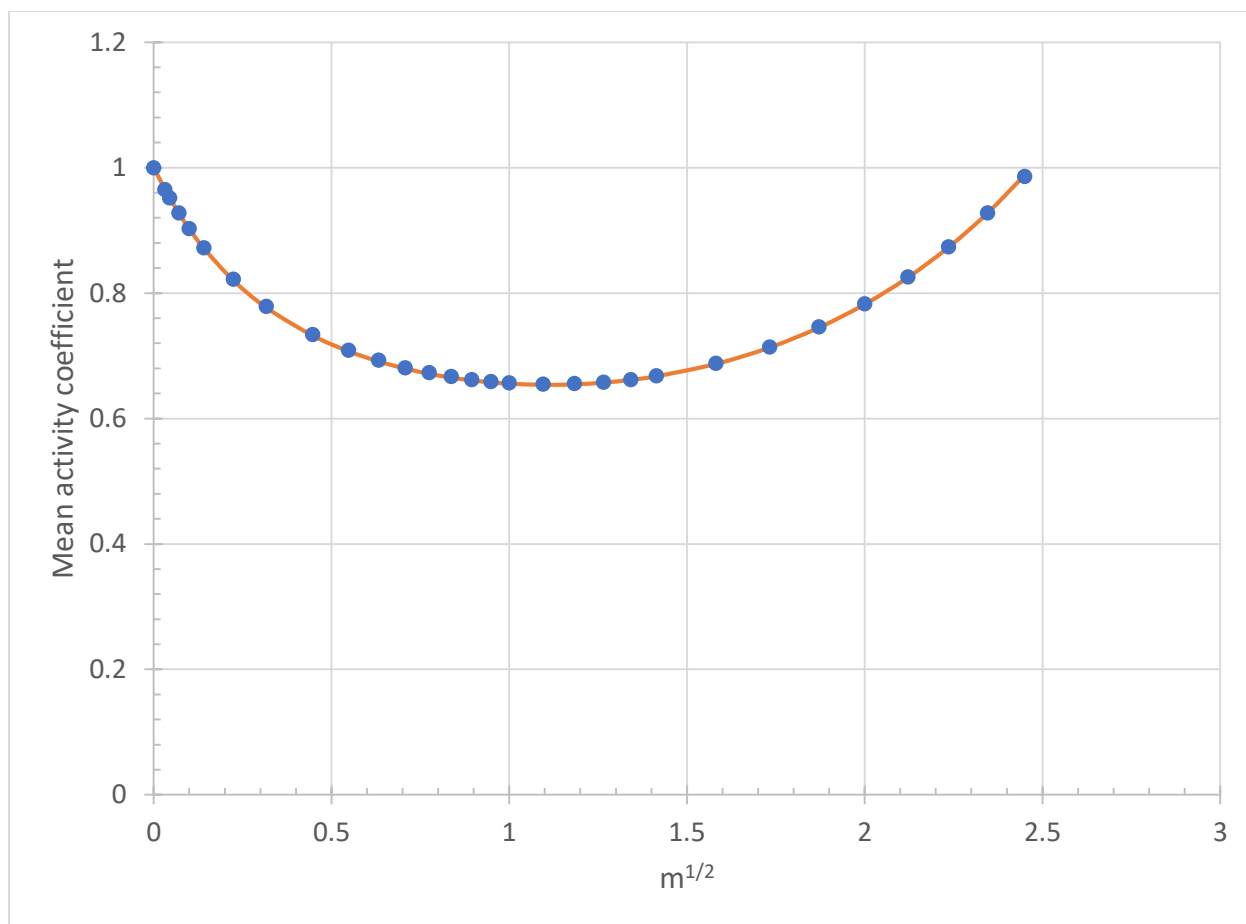
Figure 2.7. Pitzer model (line) and experimental activity coefficient data of NaCl (circles)

Figure 2.7 shows the fit of the model to the data for NaCl. The Pitzer model is very accurate, with an error of less than 1 %, in the entire molality range. However, the Pitzer model is very complicated, with many ion interaction parameters that have to be determined experimentally.

2.2.7. Applications

The SIT model has been used to model heavy metals in the environment and CO_2 storage. Powell et al. (2005) collected data of Hg^{2+} ion complexation with various anions such as Cl^- and OH^- and used the SIT model to extrapolate the complexation equilibrium constants to zero ionic strength. Based on this, they proposed recommended values for the equilibrium constants at 25 °C. They repeated this analysis for Cu^{2+} (Powell et al., 2007), and Pb^{2+} (Powell et al., 2009). A similar

approach was used by Kirby et al. (2018) to determine the stability constants of UO_2^{2+} complexes with acetate.

Powell et al. (2007) used the SIT model to evaluate the chemical speciation of copper in the environment. They found that the blue pentahydrate, $CuSO_4.5H_2O$, is the equilibrium form of solid copper(II) sulphate under the majority of environmental circumstances. Because of this salt's high solubility (>2 mol dm^{-3} at 25 °C in water, which rises sharply with temperature), Cu(II) equilibria in natural waters won't be much impacted.

The SIT model and the Pitzer model were used to evaluate the solubility of $MgCO_3$ (De Visscher et al. 2012) and $CaCO_3$ (De Visscher and Vanderdeelen, 2012) in water. They used the models to calculate the solubility constants of the carbonates as well as the acid-base chemistry of CO_2-carbonate. Matyskin (2016) used the SIT model to evaluate the solubiltiy of radium sulfate and radium carbonate in NaCl solutions of different ionic strengths. They found that an extra term proportional to $I^{1.5}$ was needed to accurately analyze the data.

The Pitzer model has been used to simulate the production of brines, to estimate the evaporation of salt water, and to assess the solubilities of carbonates in water.

Keller et al. (2021) used the Pitzer model to predict the crystallization of salt during evaporation of seawater. The electroneutrality condition was used to compute the molality of the single anion, Cl. The experimental artificial seawater solutions were examined for Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-}.

In order to determine the accuracy of the ion chromatography analysis, many test solutions with known compositions were measured.

The relative ion molality uncertainty was found to be less than 2% for Na^+ and K^+, less than 6% for Ca^{2+} and Mg^{2+}, and less than 7% for SO_4^{-2} and Cl^-. Next, model predictions were compared to the experimental data. Model predictions and experimental data of the ions' molalities in solution during the dynamic evaporation process were compared. Plots were produced to show the areas where the salts are predicted to precipitate. The Pitzer model predicted the data well for ionic strengths below 10 mol kg^{-1} but important deviations were found for ionic strengths above 10 mol kg^{-1}.

Li et al. (2019) studied the separation of $SrCl_2$ from $CaCl_2$ for the production of pure $SrCl_2$ from solar ponds on the Qinhai-Tibet plateau in China. They used the isothermal dissolution equilibrium technique to study the phase equilibria of the system $CaCl_2 + SrCl_2 + H_2O$ at 288.15 K. It was found that a solid solution $(Ca,Sr)Cl_2$ was produced at this temperature. Using findings from the literature, the Pitzer model was created for the system $CaCl_2 + SrCl_2 + H_2O$ between 288.15 K and 373.15 K. For the model, it was assumed that the precipitated solid is an ideal solid solution. The temperature dependence equations for the mixing parameters $\theta_{Ca,Sr}$ and $\psi_{Ca,Sr,Cl}$ were constructed across the temperature range 288.15 – 373.15 K. The experimental solubility data from this study's experiments and those from the literature show an excellent agreement with the model for mixed systems. Afterwards, brine separation and re-crystallization were computer simulated using the phase diagram and Pitzer model in the temperature range 288.15 – 373.15 K.

Accurate chemical speciation models are important for predicting the distribution of chemical species in aqueous solutions, particularly in seawater. Humphries et al. (2022) used literature data of the electromotive force (EMF) of a Harned cell in artificial seawaters with known composition to test existing models based on the Pitzer formalism. Harned cells measure the activity of HCl electrochemically with a platinum hydrogen electrode and a silver/silver chloride electrode. Humphries et al. found that existing models do not yet agree with the experimental data and lack uncertainty estimates, which hampers their applications and further development. To address this issue, the models of Waters and Millero (2013), Clegg and Whitfield (1995) were implemented within a generalised treatment of uncertainties and tested with EMF data. They found that the total uncertainties for calculated EMFs were dominated by just a few contributions. They concluded that the accuracy of the models can likely be improved, and they made recommendations for further work. The study also showed that standard EMFs used in the calibration of the marine 'total' pH scale can be accurately predicted with only slight modification to the original models, suggesting that they can contribute to the extension of the scale to lower salinities.

2.2.8. Models from Liquid Mixture Thermodynamics

Electrolyte solutions can also be described thermodynamically as liquid mixtures. The difference is that liquid mixture thermodynamics does not distinguish between solvent and solutes, and it uses

mole fraction instead of molality. The main electrolyte models of this type are electrolyte-NRTL and electrolyte-UNIQUAC.

The electrolyte-NRTL model (Bollas et al., 2008) is an extension of the NRTL model (Renon and Prausnitz, 1968). It combines short-range ion interaction terms from the NRTL model with a Debye-Huckel term form the Pitzer model and an additional correction term known as the Born term.

The electrolyte-UNIQUAC model (Thomsen, 2005) is an extension of the UNIQUAC model (Abrams and Prausnitz, 1975). It combines the UNIQUAC model with a Debye-Huckel term similar to the one from the Pitzer model. It does not include a Born term.

Because of the very different approach, these models are beyond the scope of the current thesis.

2.2.9. Knowledge gap

When two ions connect chemically to generate a new species in aqueous solutions, it is known as ion pairing. When one or both of the ions are monovalent, ion pairing is weak, but it is more evident when neither ion is monovalent. Ion pairing lowers the activity of the participating ions and lowers the solution's ionic strength. Ion pairing is not taken into consideration by either the SIT model or the Pitzer model. Ion pairing, in these models, is viewed as an interaction between free ions that lowers the activity coefficients of the involved ions without changing their molalities. As a result, in situations where ion pairing is prominent, these models overestimate the ionic strength.

An expansion of the SIT model was suggested in an earlier work (De Visscher, 2022). Without significantly impacting the complexity, the expansion significantly increased the model's accuracy. The present study's goals are to include ion pairing in the model and verify its accuracy in describing the activity coefficient of electrolytes that form ion pairs, with a focus on 2-2 electrolytes in particular because they frequently form relatively potent ion pairs.

Chapter 3. Model development

3.1. The SIT model and its extension

As discussed in Section 2.2.5, the ion activity coefficient according to the Specific Ion Theory (SIT) model is:

$$\log \gamma_M = -Z_M^2 \, \frac{A\sqrt{I}}{1 + 1.5\sqrt{I}} + \Sigma_a \, \varepsilon_{Ma} \cdot m_a \quad (3\text{-}1)$$

$$\log \gamma_X = - Z_X^2 \, \frac{A\sqrt{I}}{1 + 1.5\sqrt{I}} + \Sigma_c \, \varepsilon_{cX} \cdot m_c \quad (3\text{-}2)$$

This is based on the following equation for the excess Gibbs free energy of the solution:

$$\frac{G_M^E}{RT} = \frac{2A\ln 10}{(1.5)^3}\left(-\left(1-1.5\sqrt{I}\right)^2 + 1 - 2\ln\left(1+1.5\sqrt{I}\right)\right) + \ln 10 \cdot \sum_c \sum_a m_c m_a \varepsilon_{ca} \quad (3\text{-}3)$$

where c and a are all the cations and anions in the solution, respectively.

The excess Gibbs free energy is used to compute an ion's activity coefficient in the approach shown below:

$$\left(\frac{\partial G_M^E}{\partial m_i}\right)_{m_j; j \neq i} = RT \ln \gamma_i \quad (3\text{-}4)$$

De Visscher (2022) established the Extended Specific Ion theory (ESIT) model. The excess Gibbs free energy comes from:

$$\frac{G_M^E}{RT} = \frac{2A\ln 10}{(1.5)^3}\left(-\left(1-1.5\sqrt{I}\right)^2 + 1 - 2\ln\left(1+1.5\sqrt{I}\right)\right)$$

$$+ \ln 10 \left(\sum_{i=1}^{n-1}\sum_{j=i+1}^{n} m_i m_j \varepsilon_{ij} + \sum_{i=1}^{n}\sum_{\substack{j=1 \\ j \neq i}}^{n} m_i^2 m_j \varepsilon_{iij} + \sum_{i=1}^{n-2}\sum_{j=i+1}^{n-1}\sum_{k=j+1}^{n} m_i m_j m_k \varepsilon_{ijk} \right) \quad (3\text{-}5)$$

Again, the excess Gibbs free energy is used to compute an ion's activity coefficient with eq. (3-4). This results in the equation shown below:

$$\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1+1.5\sqrt{I}} + \sum_{\substack{j=1 \\ j \neq i}}^{n} m_j \varepsilon_{ij} + 2\sum_{\substack{j=1 \\ j \neq i}}^{n} m_i m_j \varepsilon_{iij} + \sum_{\substack{j=1 \\ j \neq i}}^{n} m_j^2 \varepsilon_{jji} + \sum_{\substack{j=1 \\ j \neq i}}^{n-1} \sum_{\substack{k=j+1 \\ k \neq i}}^{n} m_j m_k \varepsilon_{ijk} \quad (3\text{-}6)$$

Charge neutrality prevents the estimation of ε_{iij} and ε_{ijj} independently. Consequently, it is assumed that:

$$\varepsilon_{iij} = \varepsilon_{jji} \quad (3\text{-}7)$$

De Visscher (2022) proposed the following equation for ternary parameters to reduce the number of adjustable parameters:

$$\varepsilon_{ijk} = \varepsilon_{iij} + \varepsilon_{iik} + \varepsilon_{jjk} \quad (3\text{-}8)$$

Cations in aqueous solution can associate with anions, to form ion pairs. Ion pairing can be driven by electrostatic forces or by covalent bonding (complexation) (Marcus and Hefter, 2006). Ion pairs are at equilibrium with the free ions in solution, which can be described by an equilibrium constant as shown in the next section.

3.2. Ion Pairing

In an electrolyte CA, ion pairing is thought to cause the following reaction:

$$C^+(\text{aq}) + A^-(\text{aq}) \rightleftharpoons CA(\text{aq})$$
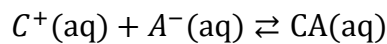
With equilibrium constant

$$K = \frac{a_{CA^0}}{a_C \cdot a_A} = \frac{\gamma_{CA} m_{CA^0} / m°}{\gamma_C m_C / m° \cdot \gamma_A m_A / m°} \quad (3\text{-}9)$$

where CA^0 refers to the ion pair CA in aqueous solution. For simplicity of use in computations, a constant in inverse molality units (kg/mol) is created:

$$K_A = \frac{K}{m°} = \frac{\gamma_{CA} m_{CA^0}}{\gamma_C m_C \cdot \gamma_A m_A} \quad (3\text{-}10)$$

The issue with ion pairing is that the species' molalities and accompanying activity coefficients don't match up with the apparent values based on the stoichiometric additions of electrolytes to the solution's 1 kg of water. The real molalities of C and A are as follows when $m_{C,app}$ and $m_{A,app}$ are defined as the stoichiometric quantities of cation and anion supplied to 1 kg of water:

$$m_C = m_{C,app} - m_{CA^0} \quad (3\text{-}11)$$

$$m_A = m_{A,app} - m_{CA^0} \quad (3\text{-}12)$$

Given that both measure the same activity, the apparent activity coefficients are computed from the real activity coefficients:

$$a_C = \gamma_C m_C = \gamma_{C,app} m_{C,app} \quad (3\text{-}12)$$

$$a_A = \gamma_A m_A = \gamma_{A,app} m_{A,app} \quad (3\text{-}13)$$

Hence:

$$\gamma_C = \frac{\gamma_{C,app} m_{C,app}}{m_C} \quad (3\text{-}14)$$

$$\gamma_A = \frac{\gamma_{A,app} m_{A,app}}{m_A} \quad (3\text{-}15)$$

The new species CA may be nonideal and should be introduced in the SIT model for calculating the activity coefficient. For a mixture of cations C, anions A, and ion pairs CA, the activity coefficients are calculated with eq. (3-6) as:

$$\log\gamma_C = -\frac{Az_C^2\sqrt{I}}{1+1.5\sqrt{I}} + m_A\varepsilon_{CA} + m_{CA}\varepsilon_{C(CA)} + 2m_C\left(m_A\varepsilon_{CCA} + m_{CA}\varepsilon_{CC(CA)}\right)$$
$$+m_A^2\varepsilon_{CAA} + m_{CA}^2\varepsilon_{C(CA)(CA)} + m_A m_{CA}\varepsilon_{CA(CA)} \quad (3\text{-}16)$$

$$\log\gamma_A = -\frac{Az_A^2\sqrt{I}}{1+1.5\sqrt{I}} + m_C\varepsilon_{CA} + m_{CA}\varepsilon_{A(CA)} + 2m_A\left(m_C\varepsilon_{CAA} + m_{CA}\varepsilon_{AA(CA)}\right)$$
$$+m_C^2\varepsilon_{CCA} + m_{CA}^2\varepsilon_{A(CA)(CA)} + m_C m_{CA}\varepsilon_{CA(CA)} \quad (3\text{-}17)$$

$$\log\gamma_{CA} = -\frac{Az_{CA}^2\sqrt{I}}{1+1.5\sqrt{I}} + m_C\varepsilon_{C(CA)} + m_A\varepsilon_{A(CA)} + 2m_{CA}\left(m_C\varepsilon_{C(CA)(CA)} + m_A\varepsilon_{A(CA)(CA)}\right)$$
$$+m_C^2\varepsilon_{CC(CA)} + m_A^2\varepsilon_{AA(CA)} + m_C m_A\varepsilon_{CA(CA)} \quad (3\text{-}18)$$

Ion relationships in the present investigation are restricted to electrically neutral ion pairs. In the last equation, $z_{CA} = 0$ so the Debye-Huckel term is zero as well, and eq. (3-18) reduces to:

$$\log\gamma_{CA} = m_C\varepsilon_{C(CA)} + m_A\varepsilon_{A(CA)} + 2m_{CA}\left(m_C\varepsilon_{C(CA)(CA)} + m_A\varepsilon_{A(CA)(CA)}\right)$$
$$+m_C^2\varepsilon_{CC(CA)} + m_A^2\varepsilon_{AA(CA)} + m_C m_A\varepsilon_{CA(CA)} \quad (3\text{-}19)$$

Equations (3-16) and (3-17) include the molalities of ion pair CA and how they affect the activity coefficients of ions C and A. As a result, interaction parameters like $\varepsilon_{I(CA)}$, $\varepsilon_{I(CA)}$, $\varepsilon_{II(CA)}$, etc. are introduced. It is assumed that all ion-ion pair interactions are governed by the ion's contribution to the ionic strength in order to prevent the proliferation of adjustable parameters.

To do this, the parameters $\varepsilon_{I(CA)}$, $\varepsilon_{I(CA)(CA)}$, and $\varepsilon_{II(CA)}$ are defined, and their relationships with other parameters, such as $\varepsilon_{C(CA)}$, etc., are inferred from their placement in the terms of eq. (3-19),

as these terms must have the same numerical values, regardless of whether they are calculated based on ion molalities or ionic strengths. This means that for the parameter $\varepsilon_{I(CA)}$:

$$
\begin{aligned}
\log \gamma_{CA} &= -\frac{Az_{CA}^2\sqrt{I}}{1+1.5\sqrt{I}} + \mathbf{m_C \varepsilon_{C(CA)}} + m_A\varepsilon_{A(CA)} + 2m_{CA}\left(m_C\varepsilon_{C(CA)(CA)} + m_A\varepsilon_{A(CA)(CA)}\right)\\
&+ m_C^2\varepsilon_{CC(CA)} + m_A^2\varepsilon_{AA(CA)} + m_C m_A\varepsilon_{CA(CA)}\\
&= -\frac{Az_{CA}^2\sqrt{I}}{1+1.5\sqrt{I}} + \frac{\mathbf{1}}{\mathbf{2}}\mathbf{z_C^2 m_C \varepsilon_{I(CA)}} + m_A\varepsilon_{A(CA)} + 2m_{CA}\left(m_C\varepsilon_{C(CA)(CA)} + m_A\varepsilon_{A(CA)(CA)}\right)\\
&+ m_C^2\varepsilon_{CC(CA)} + m_A^2\varepsilon_{AA(CA)} + m_C m_A\varepsilon_{CA(CA)}
\end{aligned}
\tag{3-20}
$$

The term containing the parameters $\varepsilon_{C(CA)}$ and $\varepsilon_{I(CCA)}$ are in bold in eq. (3-20). Solving for $\varepsilon_{I(CA)}$ leads to:

$$
\varepsilon_{I(CA)} = \frac{2}{z_C^2}\varepsilon_{C(CA)} \quad (3\text{-}21)
$$

The same relationship applies to $\varepsilon_{A\,(CA)}$, in other words, $\varepsilon_{C\,(CA)} = \varepsilon_{A\,(CA)}$.
Likewise,

$$
\begin{aligned}
\log \gamma_{CA} &= -\frac{Az_{CA}^2\sqrt{I}}{1+1.5\sqrt{I}} + m_C\varepsilon_{C(CA)} + m_A\varepsilon_{A(CA)} + \mathbf{2m_{CA}}\left(\mathbf{m_C\varepsilon_{C(CA)(CA)}} + m_A\varepsilon_{A(CA)(CA)}\right)\\
&+ m_C^2\varepsilon_{CC(CA)} + m_A^2\varepsilon_{AA(CA)} + m_C m_A\varepsilon_{CA(CA)}\\
&= -\frac{Az_{CA}^2\sqrt{I}}{1+1.5\sqrt{I}} + m_C\varepsilon_{C(CA)} + m_A\varepsilon_{A(CA)} + \mathbf{2m_{CA}}\left(\frac{\mathbf{1}}{\mathbf{2}}\mathbf{z_C^2 m_C \varepsilon_{I(CA)(CA)}} + m_A\varepsilon_{A(CA)(CA)}\right)\\
&+ m_C^2\varepsilon_{CC(CA)} + m_A^2\varepsilon_{AA(CA)} + m_C m_A\varepsilon_{CA(CA)}
\end{aligned}
\tag{3-22}
$$

Now the bold terms containing $\varepsilon_{C(CA)(CA)}$ and $\varepsilon_{I(CA)(CA)}$ must be the same. This leads to:

$$
\varepsilon_{I(CA)(CA)} = \frac{2}{z_C^2}\varepsilon_{C(CA)(CA)} \quad (3\text{-}23)
$$

And because of eq. (3-7), we also find:

$$\varepsilon_{I(CA)(CA)} = \frac{2}{z_C^2} \varepsilon_{CC(CA)} \quad (3\text{-}24)$$

Finally, based on:

$$\log \gamma_{CA} = -\frac{Az_{CA}^2 \sqrt{I}}{1+1.5\sqrt{I}} + m_C \varepsilon_{C(CA)} + m_A \varepsilon_{A(CA)} + 2m_{CA} \left(m_C \varepsilon_{C(CA)(CA)} + m_A \varepsilon_{A(CA)(CA)} \right)$$
$$+ \mathbf{m_C^2 \varepsilon_{CC(CA)}} + m_A^2 \varepsilon_{AA(CA)} + m_C m_A \varepsilon_{CA(CA)}$$
$$= -\frac{Az_{CA}^2 \sqrt{I}}{1+1.5\sqrt{I}} + m_C \varepsilon_{C(CA)} + m_A \varepsilon_{A(CA)} + 2m_{CA} \left(m_C \varepsilon_{C(CA)(CA)} + m_A \varepsilon_{A(CA)(CA)} \right) \quad (3\text{-}25)$$
$$+ \frac{1}{4} \mathbf{z_C^4 m_C^2 \varepsilon_{II(CA)}} + m_A^2 \varepsilon_{AA(CA)} + m_C m_A \varepsilon_{CA(CA)}$$

and eq. (3-7), we find:

$$\varepsilon_{II(CA)} = \frac{4}{z_C^4} \varepsilon_{CC(CA)} = \frac{4}{z_C^4} \varepsilon_{C(CA)(CA)} \quad (3\text{-}26)$$

Based on eq. (3-8) it would be expected that

$$\varepsilon_{CA(CA)} = \varepsilon_{CCA} + \varepsilon_{CC(CA)} + \varepsilon_{AA(CA)} \quad (3\text{-}27)$$

However, the first term of this equation is between ions, and the other two terms are between ions and ion pairs. It was decided to keep only the interaction terms between ions and ion pairs. In the case that C and A have the same charge, this leads to:

$$\varepsilon_{CA(CA)} = \varepsilon_{CC(CA)} + \varepsilon_{AA(CA)} = \frac{z_i^4}{2} \varepsilon_{II(CA)} \quad (3\text{-}28)$$

where i is C or A.

These substitutions applied to eqs. (3-16)-(3-18) lead to the following equations:

$$\log \gamma_C = -\frac{Az_C^2\sqrt{I}}{1+1.5\sqrt{I}} + m_A\varepsilon_{CA} + \frac{1}{2}\varepsilon_{I(CA)}\left[z_C^2 m_{CA}\right] + \varepsilon_{CCA}\left[2m_A m_C + m_A^2\right]$$
$$+\frac{1}{4}\varepsilon_{II(CA)}\left[m_{CA}z_C^4\left(2m_A + m_{CA} + 2m_C\right)\right] \qquad (3\text{-}29)$$

$$\log \gamma_A = -\frac{Az_A^2\sqrt{I}}{1+1.5\sqrt{I}} + m_C\varepsilon_{CA} + \frac{1}{2}\varepsilon_{I(CA)}\left[z_A^2 m_{CA}\right] + \varepsilon_{CAA}\left[2m_A m_C + m_C^2\right]$$
$$+\frac{1}{4}\varepsilon_{II(CA)}\left[m_{CA}z_A^4\left(2m_A + m_{CA} + 2m_C\right)\right] \qquad (3\text{-}30)$$

$$\log \gamma_{CA} = -\frac{Az_{CA}^2\sqrt{I}}{1+1.5\sqrt{I}} + \frac{1}{2}\varepsilon_{I(CA)}\left[m_C z_C^2 + m_A z_A^2\right]$$
$$+\frac{1}{2}\varepsilon_{II(CA)}\left[m_{CA}m_C z_C^4 + m_{CA}m_A z_A^4 + \frac{m_C^2 z_C^4}{2} + \frac{m_A^2 z_A^4}{2} + m_C m_A z_C^4\right] \qquad (3\text{-}31)$$

3.3. Modified Molality Scale

Inherent nonlinearity exists in the molality scale. The fact that a solution's molality approaches to infinity when the solvent concentration tends to zero makes this obvious. The modified molality scale m_i' (eq. 3-32), which is expressed in moles of i per kg of solution (as opposed to kg of solvent in the case of molality), can be used to calculate the abundance of a species that lacks this characteristic.

Using all abundances represented in moles per kg solution, a study was performed to examine the impact of the molality scale's nonlinearity. The following are the conversion formulae for modified molality m_i', concentration c_i , and molality m_i:

$$m_i' = \frac{m_i}{1+\sum_j M_j m_j} \qquad (3\text{-}32)$$

$$c_i = \frac{m_i \rho_{sol}}{1+\sum_j M_j m_j} \qquad (3\text{-}33)$$

where ρ_{sol} is the specific gravity of the solution (in kg/L) and M_j is the molar mass of chemical j in kg/mol.

In an early study, it was discovered that the modified molality scale m' expressed in mol per kg solution tended to be more accurate than the normal molality scale m (mol per kg water) for the SIT model expanded with a second-order factor (De Visscher, 2022). This is due to the fact that tiny changes in composition at high molality (m > 15 mol/kg) result in significant changes in molality. When the solute's mole fraction trends toward 1, the molality of miscible compounds theoretically increases to infinity.

The equations above describe the link between modified molality and standard molality. The reverse relationship is:

$$m_i = \frac{m'_i}{1 - \sum_j M_j m'_j} \quad (3\text{-}34)$$

where M_j is the chemical j's molar mass (kg/mol)

The relationships between the activity coefficient i in the regular molality scale and the activity coefficient i in the modified molality scale can be calculated by mandating that the activity coefficients in the two molality scales must represent the same activity (or the same chemical potential):

$$\gamma'_i = \gamma_i \left(1 + \sum_j M_j m_j \right) = \frac{\gamma_i}{1 - \sum_j M_j m'_j} \quad (3\text{-}35)$$

$$\gamma_i = \gamma'_i \left(1 - \sum_j M_j m'_j \right) = \frac{\gamma'_i}{1 + \sum_j M_j m_j} \quad (3\text{-}36)$$

3.4. Data Analysis Methodology

3.4.1. Parameter estimation of ESIT model without ion pairing

The activity coefficient of an ion i in aqueous solution according to the ESIT model is calculated as follows (Section 3.1):

$$\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1+1.5\sqrt{I}} + \sum_{\substack{j=1 \\ j\neq i}}^{n} m_j \varepsilon_{ij} + 2\sum_{\substack{j=1 \\ j\neq i}}^{n} m_i m_j \varepsilon_{iij} + \sum_{\substack{j=1 \\ j\neq i}}^{n} m_j^2 \varepsilon_{jji} + \sum_{\substack{j=1 \\ j\neq i}}^{n-1} \sum_{\substack{k=j+1 \\ k\neq i}}^{n} m_j m_k \varepsilon_{ijk} \quad (3\text{-}37)$$

The data analysis is limited to single electrolytes, i.e., with one cation and one anion. In that case, with one counter ion j, the equation simplifies to:

$$\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1+1.5\sqrt{I}} + m_j \varepsilon_{ij} + 2 m_i m_j \varepsilon_{iij} + m_j^2 \varepsilon_{jji} \quad (3\text{-}38)$$

In the case of 1-1 and 2-2 electrolytes, $m_i = m_j$ and the equation can be written as:

$$\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1+1.5\sqrt{I}} + m\,\varepsilon_{ij} + 2m^2 \varepsilon_{iij} + m^2 \varepsilon_{jji} \quad (3\text{-}39)$$

where $m = m_i = m_j$. Because

$$\varepsilon_{iij} = \varepsilon_{jji} \quad (3\text{-}40)$$

the equation can be further simplified to:

$$\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1+1.5\sqrt{I}} + m\,\varepsilon_{ij} + 3m^2 \varepsilon_{iij} \quad (3\text{-}41)$$

The activity coefficient of the counter-ion j is the same in this case. As a result, the equation can also be used to calculate the mean activity coefficient:

$$\log \gamma_\pm = -\frac{Az_i^2\sqrt{I}}{1+1.5\sqrt{I}} + m\,\varepsilon_{ij} + 3m^2\varepsilon_{iij} \quad (3\text{-}42)$$

The log of the mean activity coefficient is the Debye-Huckel term, plus a first-order term and a second-order term in the electrolyte molality. The adjustable parameters are ε_{ij} and ε_{iij}. The equation is rearranged as:

$$\log \gamma_\pm - \left(-\frac{Az_i^2\sqrt{I}}{1+1.5\sqrt{I}}\right) = m\,\varepsilon_{ij} + 3m^2\varepsilon_{iij} \quad (3\text{-}43)$$

The difference between the log of the activity coefficient and the Debye-Huckel term in the left-hand side is known as the specific interaction, i.e., the interaction that is specific to ions i and j. The data analysis is illustrated in Figure 3.1.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1	NaCl	Modified molality	1		1			0.011447	0.035089		0	#N/A	#N/A				
2		Na		Cl				4.48E-05	0.000157	#N/A	#N/A	#N/A					
3			1		1			0.99999	0.000476	#N/A	#N/A	#N/A					
4	DH slope	0.51						1342524	27	#N/A	#N/A	#N/A					
5	M	58.44 g/mol						0.60718	6.11E-06	#N/A	#N/A	#N/A					
6		0.05844 kg/mol												slope 1	slope 2	fract err	
7														0.035089	0.011447	0.001096	
8														eps MX	eps MMX	fract error	
9														0.035089	0.003816	0.001096	
10	m	gamma±	m'	I'	gamma'±	log gam	DH SIT	specific	m1	m2	gam pred	Pred specif	Deviation	slope 1	slope 2	fract err	
11	0.001	0.965	0.001	0.001	0.965056	-0.01545	-0.0154	-5E-05	0.001	1E-06	0.965247	3.51E-05	8.56E-05				
12	0.002	0.952	0.002	0.002	0.952111	-0.02131	-0.02137	6.06E-05	0.002	4E-06	0.952132	7.02E-05	9.6E-06				
13	0.005	0.928	0.005	0.005	0.928271	-0.03233	-0.0326	0.000275	0.004999	2.5E-05	0.928059	0.000176	-9.9E-05				
14	0.01	0.903	0.01	0.01	0.903528	-0.04406	-0.04434	0.000278	0.009994	9.99E-05	0.903681	0.000352	7.38E-05				
15	0.02	0.872	0.02	0.02	0.873019	-0.05898	-0.05947	0.000498	0.019977	0.000399	0.873437	0.000706	0.000208				
16	0.05	0.822	0.0499	0.0499	0.824402	-0.08386	-0.0853	0.001442	0.049854	0.002485	0.825039	0.001778	0.000335				
17	0.1	0.779	0.0994	0.0994	0.783552	-0.10593	-0.10917	0.003241	0.099419	0.009884	0.784204	0.003602	0.000361				
18	0.2	0.734	0.1977	0.1977	0.742579	-0.12926	-0.13603	0.006775	0.197689	0.039081	0.74362	0.007384	0.000609				
19	0.3	0.709	0.2948	0.2948	0.72143	-0.14181	-0.15262	0.010812	0.294831	0.086925	0.722308	0.01134	0.000528				
20	0.4	0.693	0.3909	0.3909	0.7092	-0.14923	-0.16454	0.01531	0.390863	0.152774	0.70945	0.015464	0.000153				
21	0.5	0.681	0.4858	0.4858	0.700899	-0.15434	-0.17378	0.019436	0.485805	0.236006	0.701401	0.019748	0.000311				
22	0.6	0.673	0.5797	0.5797	0.696598	-0.15702	-0.18127	0.024255	0.579674	0.336022	0.696487	0.024186	-6.9E-05				
23	0.7	0.667	0.6725	0.6725	0.694286	-0.15846	-0.18754	0.029077	0.67249	0.452243	0.6938	0.028773	-0.0003				
24	0.8	0.662	0.7643	0.7643	0.69295	-0.1593	-0.1929	0.033601	0.764269	0.584107	0.692794	0.033503	-9.8E-05				
25	0.9	0.659	0.855	0.855	0.693661	-0.15885	-0.19756	0.03871	0.855029	0.731074	0.693118	0.03837	-0.00034				
26	1	0.657	0.9448	0.9448	0.695395	-0.15777	-0.20168	0.043908	0.944787	0.892622	0.694533	0.043369	-0.00054				
27	1.2	0.655	1.1214	1.1214	0.700934	-0.15432	-0.20865	0.054323	1.121361	1.257451	0.699995	0.053741	-0.00058				
28	1.4	0.656	1.2941	1.2941	0.709671	-0.14894	-0.21437	0.065429	1.29412	1.674747	0.708285	0.064579	-0.00085				
29	1.6	0.658	1.4632	1.4632	0.719526	-0.14295	-0.21919	0.07624	1.463186	2.140914	0.718875	0.075848	-0.00039				

Sheet tabs: NaCl | AgNO3 | HF | HCl | HBr | HI | HClO4 | HNO3 | LiOH | LiCl | LiBr | LiI | LiClO4 | LiNO3 ...

Figure 3.1 Screenshot of data analysis of activity coefficient data without ion pairing in Excel

The top left corner contains data such as the molar mass and the Debye-Huckel slope. The main calculations start at row 11 as indicated below.

Columns A and B are the data from the literature, expressed in regular molality (mol per kg water). In column C, m' is the modified molality (mol per kg solution), which is m /(1+ molar mass . m), as per eq. (3-32). Based on this, the ionic strength in modified molality is calculated in column D. In column E, gamma' is the activity coefficient in modified molality, which is gamma (1+ molar mass . m) as per eq. (3-35). In column F, the log of this activity coefficient is calculated.

DH SIT in column G is the Debye-Huckel term in modified molality, calculated as

$$\left(-\frac{Az_i^2 \sqrt{I}}{1+1.5\sqrt{I}} \right) \quad (3\text{-}44)$$

The difference between log gamma (column F) and DH SIT (column G), calculated in column H is the specific ion interaction ("specific").

The Columns H, I, and J contain the data needed to calculate the interaction parameters by linear regression. Column H (specific interaction) is the dependent variable. The next two columns are m' (modified molality) and m'^{2} (square of modified molality). The regression is based on the equation:

$$\log \gamma_{\pm} - \left(-\frac{Az_i^2 \sqrt{I}}{1+1.5\sqrt{I}} \right) = m\,\varepsilon_{ij} + 3m^2\varepsilon_{iij} \quad (3\text{-}45)$$

It follows that the regression coefficients are ε_{ij} and $3\varepsilon_{iij}$. The regression has no constant term.

The regression is calculated with the Excel function LINEST in cells H1 to L6. The expression is:
{=LINEST(H11:H39,I11:J39,FALSE,TRUE)}

The outside brackets are obtained by pressing ctrl+alt+enter while selecting cells H1 to L6. This indicates that the cells H1 to L6 are used as a block of output data.

The parameters of the function LINEST are the dependent variable (H11:H39), the independent variables (I11:J39), the existence of a constant term (FALSE) and the inclusion of statistics in the output (TRUE).

The first slope (ε_{ij}) is given in cell I1, and the second slope ($3\varepsilon_{iij}$) in cell H1.

For convenience, the parameter values are repeated in cells N7 and O7 and the values of ε_{ij} and ε_{iij} are calculated in cells N9 and O9.

In cell P7, the fractional error of the model is calculated from the standard error of the regression as follows. Cell I3 shows the standard error in log scale. In cell P7, this value is used to calculate the fractional error (or relative error, i.e., 1/100 of the % error):

fractional error $= 10^{(\text{standard error})} - 1$

In column K, the model predictions of the activity coefficient are given. Column L contains the model predictions of the specific ion interactions in log scale, and column M contains the difference between the experimental and predicted specific ion interaction in log scale.

The activity coefficient data were taken from Hamer and Wu (1972) for 1-1 electrolytes, and Robinson and Stokes (1959) for the other electrolytes.

3.4.2. Parameter estimation of ESIT model with ion pairing

To analyze activity coefficient data with ion pairing, represented by equilibrium constant K, thermodynamic models are used that take into account the formation of ion pairs or complexes in solution.

For the ion pair, the activity coefficient is calculated with eq. (3-37), applied to a cation C, an anion A and an ion pair (CA).

$$
\begin{aligned}
\log \gamma_{CA} = & -\frac{A z_{CA}^2 \sqrt{I}}{1+1.5\sqrt{I}} + \frac{1}{2}\varepsilon_{I(CA)}\left[m_C z_C^2 + m_A z_A^2\right] \\
& + \frac{1}{2}\varepsilon_{II(CA)}\left[m_{CA}m_C z_C^4 + m_{CA}m_A z_A^4 + \frac{m_C^2 z_C^4}{2} + \frac{m_A^2 z_A^4}{2} + m_C m_A z_C^4\right]
\end{aligned}
\tag{3-46}
$$

Because the equation is only applied to 1-1 and 2-2 electrolytes, $z_C = z_A$ and $m_C = m_A = m_{real}$ (the real free ion concentration). The equation can be simplified to:

$$\log \gamma_{CA} = -\frac{Az_{CA}^2 \sqrt{I}}{1+1.5\sqrt{I}} + \varepsilon_{I(CA)} m_{real} z_C^2 + \varepsilon_{II(CA)} \left[m_{CA} m_{real} z_C^4 + m_{real}^2 z_C^4 \right] \quad (3\text{-}47)$$

In the case of 1-1 and 2-2 electrolytes, the ion pair is electrically neutral and the Debye-Huckel term is zero.

For the free cation and the free anion, the activity coefficients are calculated as follows:

$$\log \gamma_C = -\frac{Az_C^2 \sqrt{I}}{1+1.5\sqrt{I}} + m_A \varepsilon_{CA} + \frac{1}{2} \varepsilon_{I(CA)} \left[z_C^2 m_{CA} \right] + \varepsilon_{CCA} \left[2m_A m_C + m_A^2 \right]$$

$$+ \frac{1}{4} \varepsilon_{II(CA)} \left[m_{CA} z_C^4 \left(2m_A + m_{CA} + 2m_C \right) \right] \quad (3\text{-}48)$$

$$\log \gamma_A = -\frac{Az_A^2 \sqrt{I}}{1+1.5\sqrt{I}} + m_C \varepsilon_{CA} + \frac{1}{2} \varepsilon_{I(CA)} \left[z_A^2 m_{CA} \right] + \varepsilon_{CAA} \left[2m_A m_C + m_C^2 \right]$$

$$+ \frac{1}{4} \varepsilon_{II(CA)} \left[m_{CA} z_A^4 \left(2m_A + m_{CA} + 2m_C \right) \right] \quad (3\text{-}49)$$

Only the mean activity coefficient, $\gamma_\pm$, can be determined experimentally. For 1-1 and 2-2 electrolytes, it is calculated by applying eq. (2-6) with a = c:

$$\log \gamma_\pm = \frac{\log \gamma_C + \log \gamma_A}{2} \quad (3\text{-}50)$$

This leads to:

$$\log \gamma_\pm = -\frac{A\frac{z_C^2 + z_A^2}{2} \sqrt{I}}{1+1.5\sqrt{I}} + \varepsilon_{CA} \left[\frac{m_A + m_C}{2} \right] + \frac{1}{2} \varepsilon_{I(CA)} \left[\frac{z_C^2 + z_A^2}{2} m_{CA} \right] + \varepsilon_{CCA} \left[2m_A m_C + \frac{m_C^2 + m_A^2}{2} \right]$$

$$+ \frac{1}{4} \varepsilon_{II(CA)} \left[m_{CA} \frac{z_C^4 + z_A^4}{2} \left(2m_A + m_{CA} + 2m_C \right) \right]$$

$$(3\text{-}51)$$

Next, assume $z_C = z_A$ and $m_C = m_A = m_{real}$:

$$\log \gamma_{\pm} = -\frac{A z_C^2 \sqrt{I}}{1+1.5\sqrt{I}} + \varepsilon_{CA} m_{real} + \frac{1}{2}\varepsilon_{I(CA)} z_C^2 m_{CA} + \varepsilon_{CCA}\cdot 3 m_{real}^2 + \frac{1}{4}\varepsilon_{II(CA)}\left[m_{CA} z_C^4 \left(4 m_{real} + m_{CA}\right)\right]$$

(3-52)

This forms the basis of the data analysis.

Top-left metadata block:

MgSO4	Modified molality		2		2			K	dev log	eps MX	eps MMX	
		Mg		SO4								
			1		1			191	0.003389			
DH slope	0.51							185	0.001913			
M	120.366 g/mol							180	0.000929			
	0.120366 kg/mol							178	0.000904			
K	178							sumsq	6.95E-05			

N	O	P	Q	R
0.021685	0.055664	-0.40878	0	#N/A
0.00053	0.000286	0.002207	#N/A	#N/A
0.99993	0.000904	#N/A	#N/A	#N/A
67019.8	14	#N/A	#N/A	#N/A
0.164147	1.14E-05	#N/A	#N/A	#N/A

	slope 1	slope 2	slope 3	fract err	
	-0.40878	0.055664	0.021685	0.002083	
	eps MX	eps MMX	eps II(MX)	fract error	K
	-0.40878	0.055664	0.021685	0.002083	178
coeff	coeff	coeff			
eps MX	eps MMX	eps II(MX)	gam pred	Pred specif	Deviation

Main data table (rows 10–27):

m	gammat	m'	I'	gamma't	log gam	m MX	gam MX	K	K difference	I'real	real gam	DH SIT	specific	eps MX	eps MMX	eps II(MX)	gam pred	Pred specif	Deviation	slope 1	slope 2		fract err	
0.1	0.15	0.0988	0.3952	0.151805	-0.81871	0.039734	1.003033	177.9986	-0.00137	0.236306	0.253908	-0.5735	-0.02183	0.059076	0.01047	0.031326	0.25329	-0.02289	-0.00106					
0.2	0.107	0.1953	0.7812	0.109576	-0.96029	0.080966	1.011597	177.9973	-0.0027	0.457329	0.187174	-0.68486	-0.0429	0.114332	0.039216	0.124196	0.187621	-0.04186	0.001035					
0.3	0.0874	0.2895	1.1582	0.090556	-1.04308	0.119741	1.025723	177.997	-0.00299	0.679213	0.154414	-0.75183	-0.05948	0.169803	0.086499	0.272666	0.154698	-0.05869	0.000798					
0.4	0.0756	0.3816	1.5265	0.07924	-1.10106	0.155845	1.045609	177.9967	-0.00332	0.903125	0.133935	-0.79929	-0.07382	0.225781	0.152931	0.470817	0.13401	-0.07357	0.000243					
0.5	0.0675	0.4716	1.8865	0.071562	-1.14532	0.189307	1.071544	177.9966	-0.00336	1.12924	0.119549	-0.83571	-0.08674	0.28231	0.239097	0.712992	0.119579	-0.08663	0.000108					
0.6	0.0616	0.5596	2.2383	0.066049	-1.18014	0.220223	1.103909	177.9975	-0.00248	1.357457	0.108909	-0.86503	-0.0979	0.339364	0.345505	0.993824	0.108899	-0.09794	-4.1E-05					
0.7	0.0571	0.6456	2.5824	0.061911	-1.20823	0.248709	1.14318	177.998	-0.00205	1.58758	0.100707	-0.88941	-0.10753	0.396895	0.472577	1.308248	0.100698	-0.10757	-3.9E-05					
0.8	0.0536	0.7297	2.9189	0.058761	-1.23091	0.27489	1.189937	177.9981	-0.00185	1.819369	0.094274	-0.91015	-0.11545	0.454842	0.620644	1.651507	0.094248	-0.11557	-0.00012					
0.9	0.0508	0.812	3.2481	0.056303	-1.24947	0.298889	1.244875	177.9983	-0.00166	2.052575	0.089098	-0.92812	-0.12201	0.513144	0.78995	2.019147	0.089099	-0.12201	3.72E-06					
1	0.0485	0.8926	3.5703	0.054338	-1.2649	0.320826	1.308824	177.9988	-0.00119	2.286957	0.084829	-0.94389	-0.12756	0.571739	0.980657	2.407007	0.084951	-0.12694	0.000625	-0.28347	0.510574	-0.11605	0.003949	191
1.2	0.0453	1.0485	4.1942	0.051843	-1.28531	0.358956	1.467857	177.9989	-0.00111	2.758371	0.078829	-0.97045	-0.13286	0.689593	1.426615	3.228097	0.078897	-0.13248	0.000374					
1.4	0.0434	1.1981	4.7924	0.050713	-1.29488	0.390089	1.677148	178	-1.9E-05	3.232063	0.075197	-0.9921	-0.1317	0.808016	1.958668	4.086713	0.07503	-0.13266	-0.00096					
1.6	0.0423	1.3416	5.3665	0.050446	-1.29717	0.414891	1.950661	178.0004	0.000444	3.706928	0.073031	-1.01021	-0.12629	0.926732	2.576496	4.95818	0.07276	-0.1279	-0.00161					
1.8	0.0417	1.4795	5.9178	0.050735	-1.2947	0.43388	2.307689	178.0002	0.000198	4.182328	0.071788	-1.02565	-0.1183	1.045582	3.279725	5.820384	0.071731	-0.11864	-0.00035					
2	0.0417	1.612	6.4478	0.051739	-1.28619	0.447419	2.775076	177.9997	-0.00031	4.658131	0.071617	-1.03905	-0.10594	1.164533	4.068409	6.652775	0.071719	-0.10532	0.000619					
2.5	0.0439	1.9217	7.6869	0.05711	-1.24329	0.458375	4.716119	177.997	-0.00301	5.853397	0.074999	-1.0662	-0.05874	1.463349	6.424173	8.469369	0.075309	-0.05695	0.001792					
3	0.0492	2.2041	8.8164	0.066966	-1.17415	0.436565	8.847588	178.0000	0.000718	7.070152	0.083506	-1.08737	0.009089	1.767538	9.372571	9.640919	0.083341	0.008228	-0.00086	-0.27026	0.320336	-0.0672	0.018161	191

Sheet tabs: BeSO4 version 3 | MgSO4 version 1 | MgSO4 version 2 | **MgSO4 version 3** | MnSO4 version 1 | MnSO4 version 2 | MnSO4 version 3 | NiSO4 version 1 | NiSO4 version 2 | NiSO4 ver

Figure 3.2 Screenshot of data analysis of activity coefficient data with K ion pairing (2-2) electrolyte MgSO4 (with K) in Excel:

The top left corner contains data such as the molar mass and the Debye-Huckel slope. The main calculations start at row 11 as indicated below.

Columns A and B are the data from the literature, expressed in regular molality (mol per kg water).

In column C, m' is the modified molality (mol per kg solution), which is m /(1+ molar mass . m). Based on this, in column D, the ionic strength in modified molality is calculated.

In column E, gamma' is the activity coefficient in modified molality, which is gamma (1+ molar mass . m).

In column F, the log of this activity coefficient is calculated.

Column G contains the molality of the ion pair MX. Before regression, initial guesses of the molalities are entered based on prior experience. These guesses are improved by a procedure that will be discussed below.

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Column H calculates the activity coefficient of the ion pair with eq. (3-46), based on the molalities m_{CA} and m_{real}, the charge number, and parameter $\varepsilon_{II(CA)}$. It was decided to set $\varepsilon_{I(CA)}$ equal to zero to limit the number of adjustable parameters.

Column I calculates the value of equilibrium constant K based on the molalities m_{CA} and m_{real}, and the activity coefficient γ_{CA}.

Column J calculates the difference between the calculated K and the assumed value of K, which is specified in cell B8. The assumed value of K is determined separately by trial and error, as discussed below.

Column K calculates the real ionic strength based on m_{real}.

Column L calculates the real mean activity coefficient $\gamma_\pm$ based on the experimental value of the apparent activity coefficient. It is calculated based on:

$$activity = m_{C,apparent} \cdot \gamma_{\pm,apparent} = m_{C,real} \cdot \gamma_{\pm,real} \quad (3\text{-}53)$$

therefore:

$$\gamma_{\pm,real} = \frac{m_{C,apparent} \cdot \gamma_{\pm,apparent}}{m_{C,real}} \quad (3\text{-}54)$$

Column M calculates the logarithm of the Debye-Huckel term based on the real ionic strength.

Column N calculates the log of the part of the activity coefficient that is not explained by the Debye-Huckel term, i.e., the specific ion interaction. This is the dependent variable in the regression for the data analysis.

The next three terms are the independent variables in the regression: column O for ε_{CA}, column P for ε_{CCA}, and column Q for $\varepsilon_{II(CA)}$.

Column R calculates the prediction of the activity coefficient $\gamma_\pm$.

Column S calculates a prediction of the contribution of the specific ion contribution to the logarithm of the activity coefficient.

Colum T calculates the difference between column S and column N, which is the regression error.

The regression is calculated with the Excel function LINEST in cells N1 to R6. The expression is:

{=LINEST(N11:N27,O11:Q27,FALSE,TRUE)}

Again, the outside brackets are obtained by pressing ctrl+alt+enter while selecting cells N1 to R6. This indicates that the cells N1 to R6 are used as a block of output data.

The parameters of the function LINEST are the dependent variable (N11:N27), the independent variables (O11:Q27), the existence of a constant term (FALSE) and the inclusion of statistics in the output (TRUE).

The parameters are copied in cells U9, V9, and W9 for convenience, along with the fractional error in X9 and K in Y9.

The equilibrium constant K in cell B8 and the values of m_{MX} in cells G11:G27 are obtained by trial and error. First, value of K and m_{MX} are selected randomly, starting with small values. Then the Solver was used to minimize the sum of squares of the differences between the K values in column I and the K value in cell B8 (column J, cell J9). The fractional error in cell X9 is recorded. Then, the value of K is increased and the process is repeated. If the increase of K causes a decrease of the fractional error, then K is increased further until a minimum of the fractional error is found.

Chapter 4. Results and Discussion

4.1. Results with extended SIT in modified molality scale for 1-1 electrolytes

The parameters of the extended SIT model were estimated by linear regression in Excel for 30 electrolytes reported by Hamer and Wu (1972). The results are shown in Table 4.1. The average standard error is 0.092 (9.2 %). However, this is because the error for HF is very large, more than 200 %. Without HF, the remaining electrolytes have a standard error of 0.013 (1.3 %). The error varies from 0.00075 (0.075 %) for RbF to 0.065 (6.5 %) for HI.

Table 4.1. Model parameters for 1-1 electrolytes in modified molality scale. Fit to data of Hamer and Wu (1972) for m = 0-6 mol/kg.

Electrolyte		ε_{MX}	ε_{MMX}	Relative St. Err.	St. Err. (log units)
NaCl		0.035089	0.003816	0.001096	0.000476
AgNO$_3$		-0.13006	0.005426	0.011294	0.004878
HF		-1.29295	-0.067242	2.379169	0.52881
HCl		0.125027	0.003226	0.008285	0.003583
HBr		0.147148	0.012029	0.018811	0.008094
HI		0.200535	0.018994	0.040632	0.017297
HClO$_4$		0.01120573	0.015622	0.026192	0.011229
HNO$_3$		0.093256	0.001018	0.002497	0.001083
LiOH		-0.083829	0.021076	0.034733	0.014829
LiCl		0.097811	0.004675	0.005886	0.002549
LiBr		0.115033	0.012045	0.012229	0.05279
LiI		0.214057	0.010273	0.017543	0.007553
LiClO$_4$		0.187469	0.008544	0.011788	0.005089
LiNO$_3$		0.109706	0.002187	0.024374	0.010459
NaOH		0.038675	0.011963	0.005309	0.002299
NaBr		0.059124	0.008381	0.009407	0.004066
NaI		0.051989	0.021418	0.064804	0.02727
NaClO$_4$		0.039643	0.004981	0.003695	0.001602
NaNO$_3$		-0.035385	0.003473	0.005783	0.002504
NaH$_2$PO$_4$		-0.112494	0.008317	0.005526	0.002393
KOH		0.086361	0.00562	0.022337	0.009594
KCl		0.003522	0.00393	0.004576	0.001983
KBr		0.053329	0.007151	0.002548	0.001105
KI		0.068796	0.006883	0.001408	0.000611
RbF		0.155175	0.004157	0.000752	0.000327
NaF		-0.04607	0.008837	0.001865	0.000809
NaCNS		0.078404	0.003866	0.006423	0.002781
KF		0.026403	0.004507	0.005001	0.002167

KNO$_3$	-0.14046	0.0066	0.010391	0.00449
KH$_2$PO$_4$	-0.18099	0.015719	0.005952	0.002577

Figures 4-1 to 4-4 show the fit of the model to the literature data for the following electrolytes: NaCl, AgNO$_3$, HCl, and LiOH.

Figure 4.1 Reported activity coefficient data converted to modified molality scale (circles), and prediction with extended SIT model (line), for NaCl

A very good agreement is found for the mean activity coefficient of NaCl in the entire molality range. The standard error is about 0.1 %.

Figure 4.2 Reported activity coefficient data converted to modified molality scale (circles), and prediction with extended SIT model (line), for $AgNO_3$

For $AgNO_3$, the agreement is good (1.1 % standard error), but the model overestimates the activity coefficient at molalities below 1 mol/kg, and underestimates the activity coefficient at higher molalities.

Figure 4.3 Reported activity coefficient data converted to modified molality scale (circles), and prediction with extended SIT model (line), for HCl

For HCl, the agreement between the model and the data is good (0.8 % standard error), with an overestimation at intermediate molalities.
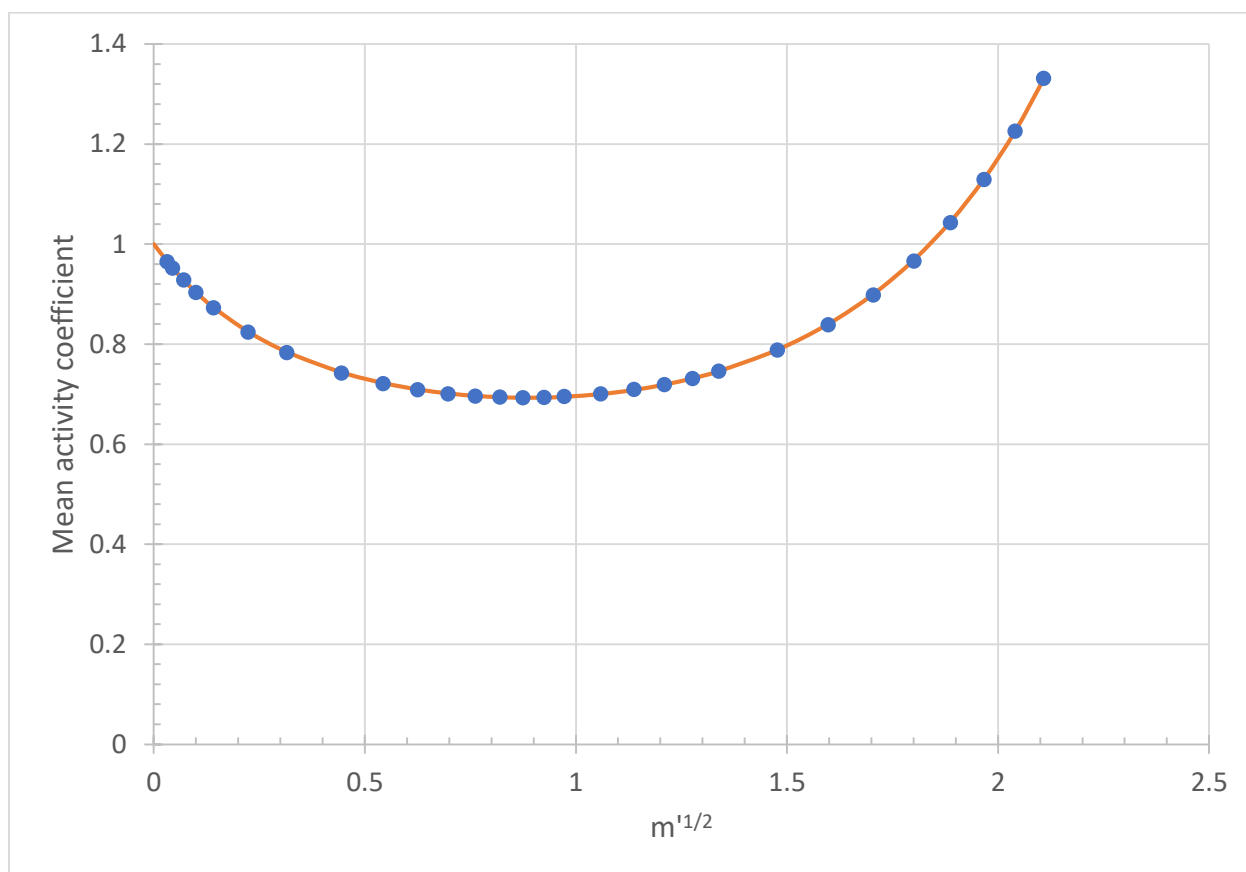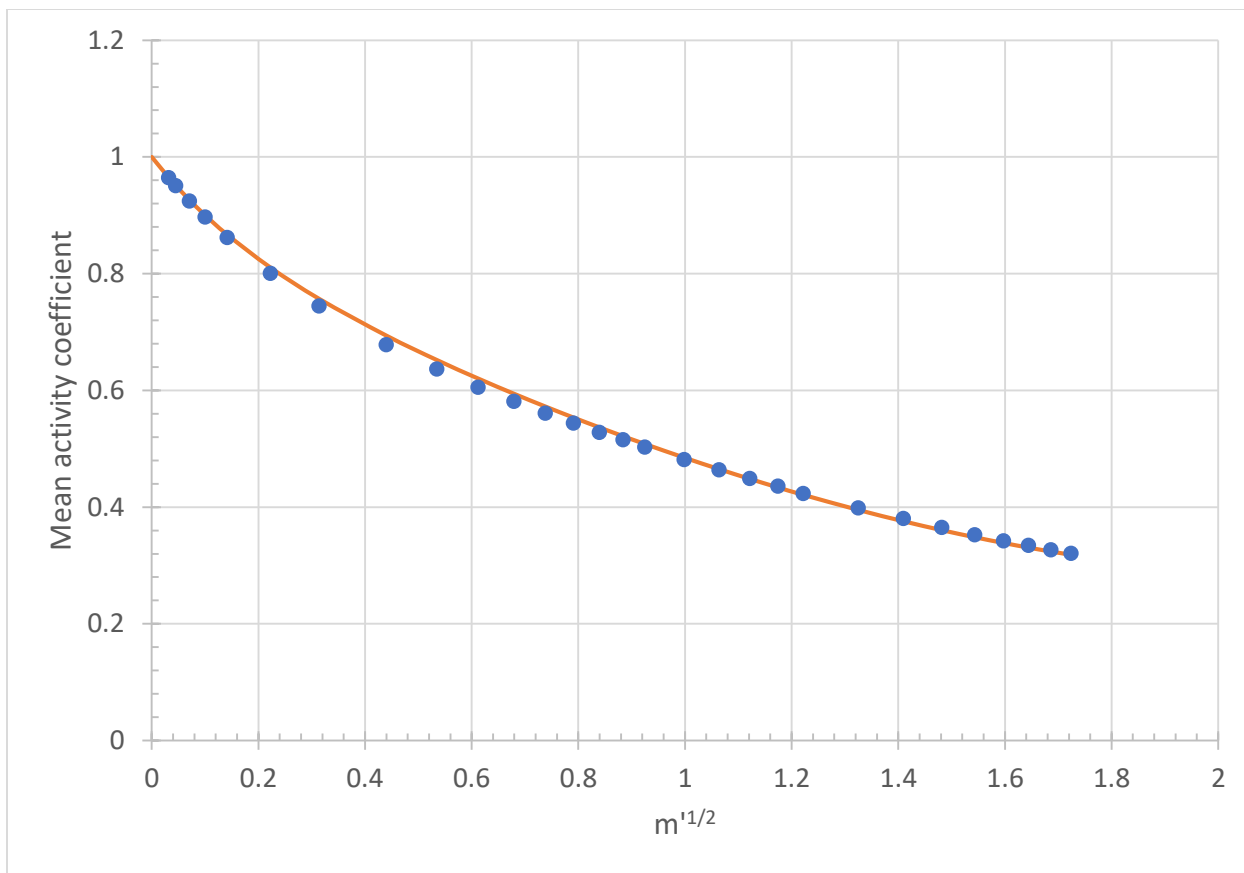
Figure 4.4 Reported activity coefficient data converted to modified molality scale (circles), and prediction with extended SIT model (line), for LiOH

For LiOH, there is a clear disagreement between the model and the data, with a standard error of about 3.5 %. The model cannot fit the lower molality dependence of the activity coefficient above 1 mol/kg

Both $AgNO_3$ and LiOH have model predictions that overestimate the activity coefficient for the square root of the molality between 0.1 and 1, i.e., a molality between 0.01 mol/kg and 1 mol/kg. This may indicate a systematic error and will be explored in later sections.

4.2. Results with extended SIT in modified molality scale for 1-2 electrolytes

The parameters of the extended SIT model were estimated by linear regression in Excel for 9 electrolytes reported by Hamer and Wu (1972). The results are shown in Table 4.2. The average

41

standard error is 0.0059 (log scale) and the average relative error is 0.0138 (1.38 %), about the same as for 1-1 electrolytes (1.3 %). The relative standard error ranges from 0.47 % to 2.15 %, indicating consistently good agreement between the model and the data.

Table 4.2 Model parameters for 1-2 electrolytes in modified molality scale. Fit to data of Hamer and Wu (1972) for m = 0-6 mol/kg.

Electrolyte		ε_{MX}	εMMX	Relative St. Err.	St. Err. (log units)
Li_2SO_4		-0.05967	0.0104	0.014792	0.006377
Na_2SO_3		-0.1305	0.01253	0.010659	0.004605
Na_2SO_4		-0.20968	0.014087	0.017643	0.007596
Na_2HPO_4		-0.20119	0.011683	0.004684	0.002029
Na_2CO_3		-0.01528	0.010284	0.009813	0.004241
K_2SO_4		-0.0513	0.117667	0.017914	0.007711
K_2HPO_4		-0.02118	0.02725	0.007596	0.0032846
Rb_2SO_4		-0.02114	0.028442	0.019592	0.008426
Cs_2SO_4		-0.0171	0.035279	0.021542	0.009256

Figure 4.5 compares the model for Li_2SO_4 with the literature data. The agreement is good in the entire molality range, but with model predictions that slightly overestimate the activity coefficient for the square root of the molality between 0.1 and 1, i.e., a molality between 0.01 mol/kg and 1 mol/kg. This is the same trend as was seen for $AgNO_3$ and LiOH in the previous section.
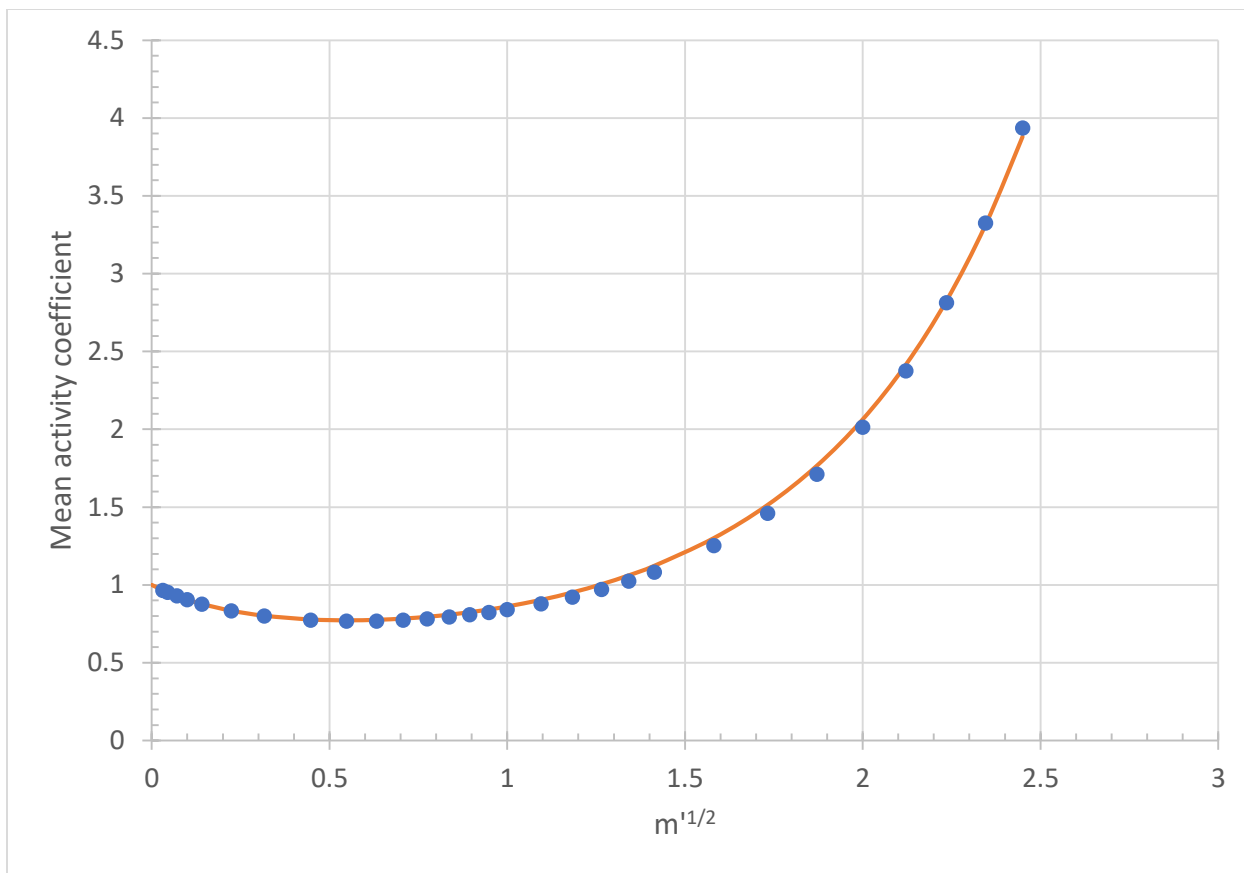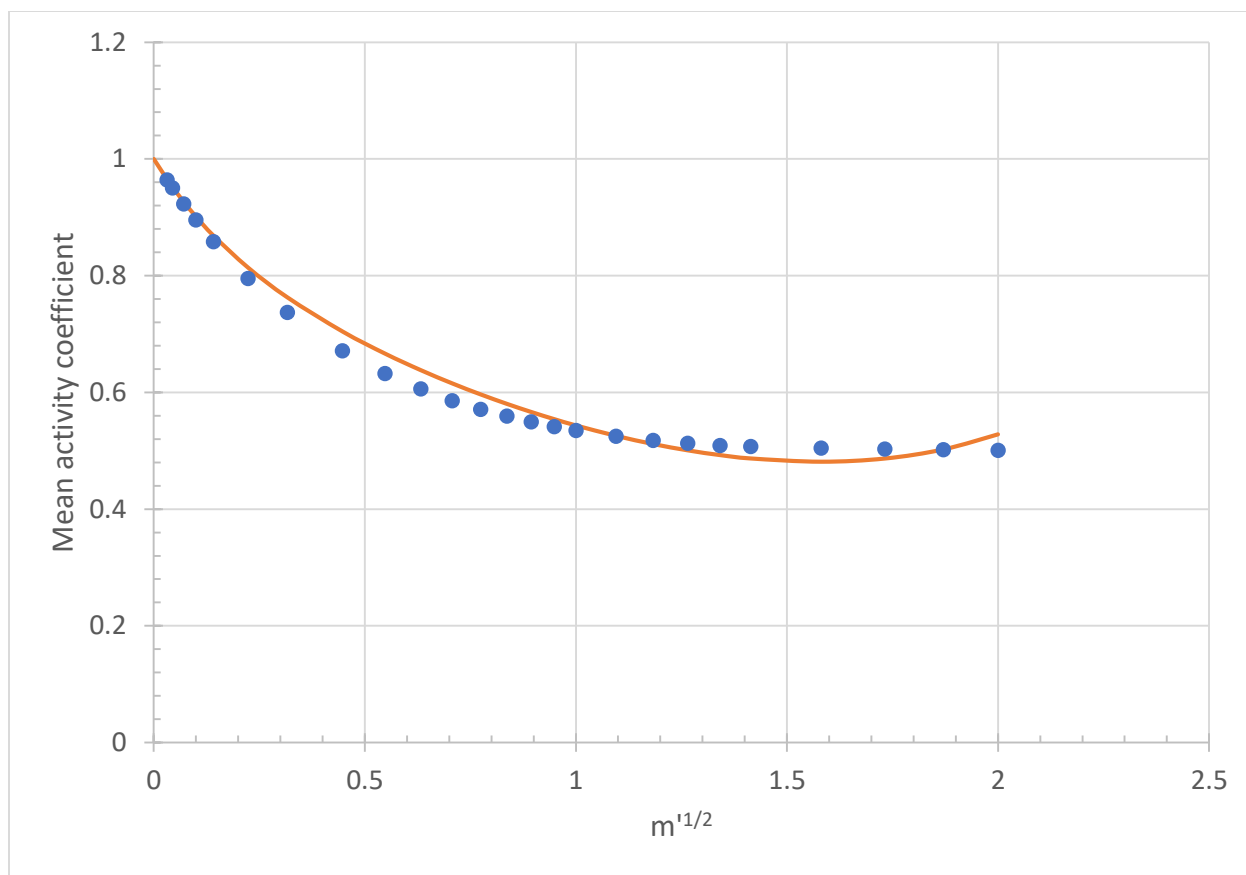
Figure 4.5 Reported activity coefficient data converted to modified molality scale (circles), and prediction with extended SIT model (line) Li_2SO_4

4.3. Results with extended SIT in modified molality scale for 2-2 electrolytes

Table 4.3 shows the parameter estimations for seven 2-2 electrolytes, all sulphates. Large negative values of ε_{MX} were found, with positive values of ε_{MMX}. The regression error was very large for all regressions. The average standard error was 0.04698 (log scale), with an average relative standard error of 0.1142 (11.42 %).

Table 4.3 Model parameters for 2-2 electrolytes in modified molality scale. Fit to data of Robinson and Stokes (1959) for m = 0-6 mol/kg.

Electrolyte		ε_{MX}	ε_{MMX}	Relative St. Err.	St. Err. (log units)
$BeSO_4$		-0.41951	0.061603	0.143102	0.058085
$MgSO_4$		-0.5156	0.076834	0.122354	0.05013
$MnSO_4$		-0.54297	0.074700	0.116401	0.04782
NiO_4		-0.64706	0.101835	0.104089	0.043004
$CuSO_3$		-0.79553	0.160801	0.099148	0.041056
$ZnSO_4$		-0.59516	0.089999	0.10848	0.045119
$CdSO_4$		-0.63098	0.097976	0.105728	0.043648

Figure 4.6 shows the model predictions for $MgSO_4$, with literature data. It is seen that the model overestimates the activity coefficient for molalities up to about 0.7 mol/kg, and underestimates the activity coefficient for molalties between 0.7 and 1.9 mol/kg. Similar trends are seen in all 2-2 electrolytes tested. It is hypothesized that this is due to ion pairing. This will be tested in the next section.
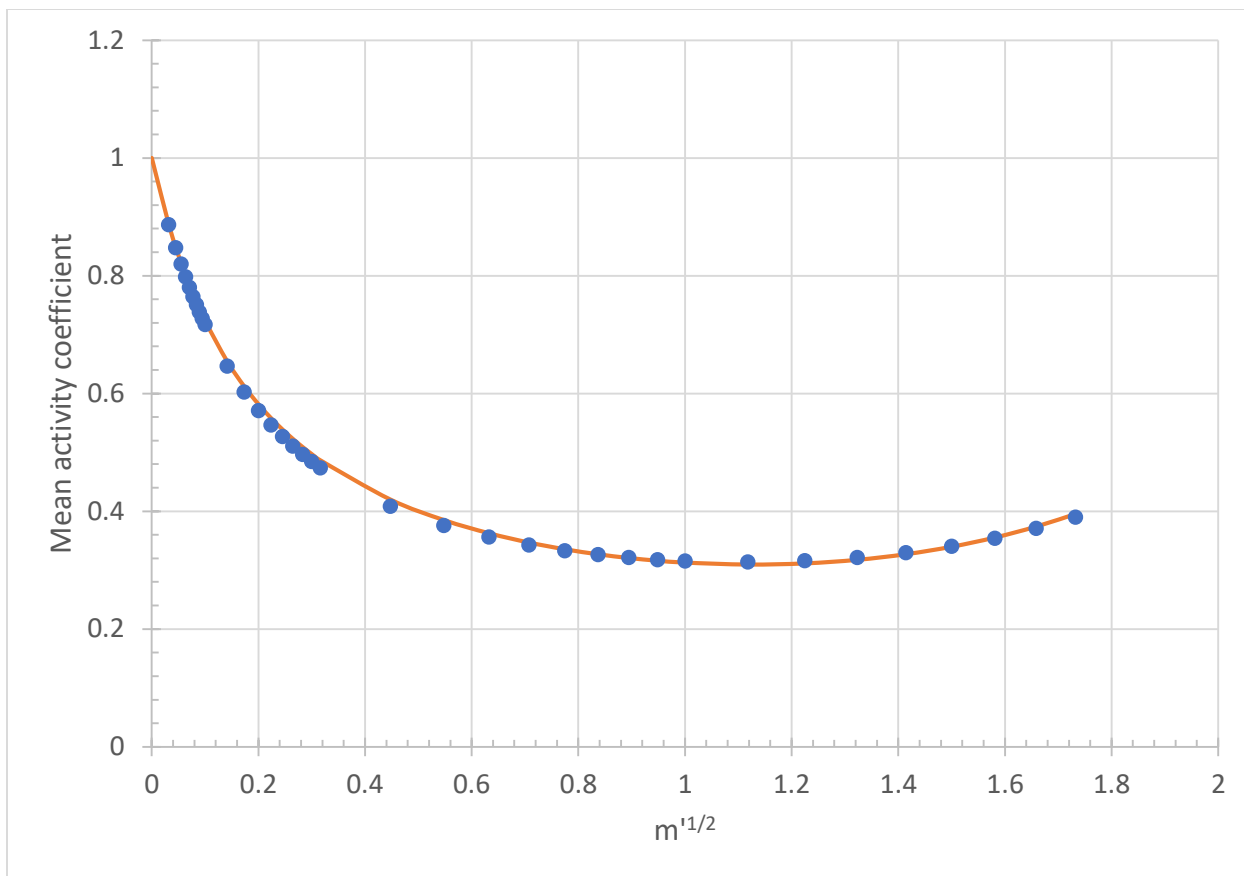
Figure 4.6 Reported activity coefficient data converted to modified molality scale (circles), and prediction with extended SIT model (line), without K, MgSO$_4$

4.4. Results with extended SIT in modified molality scale for 2-2 electrolytes with ion pairing

In Section 4.3, it was found that the fitting error of the extended SIT model is about 10 % for 2-2 electrolytes. The strong deviation at low molality indicates that the behavior deviates from the Debye-Huckel limiting slope in the limit to zero molality. But the limiting slope is based on fundamental theory that is expected to be correct. The only way to explain this is by assuming that the ionic strength deviates from the stoichiometric value, i.e., by assuming ion pairing. Furthermore, the existence of ion pairing in MgSO$_4$ has been shown experimentally by Buchner et al. (2004).

The data analysis was made in Excel. The fit to the activity coefficient data was done by linear regression with the LINEST function. The equilibrium condition of the ion pair was optimized by nonlinear least-squares with the Excel Solver, as discussed previously.

The results of the regression are shown in Table 4.4.

The average standard error was 0.00317 (log scale), with an average relative standard error of 0.000733 (0.733 %). Including K reduced the standard error of the model by more than a factor 10. Except for $CdSO_4$, the standard errors are less than 1 %.

Table 4.4 Model parameters for 2-2 electrolytes in modified molality scale. Fit to data of Robinson and Stokes (1959) for $m = 0$-6 mol/kg; with K.

Electrolyte		ε_{MX}	ε_{MMX}	$\varepsilon_{II(MX)}$	K	Relative St. Err.	St. Err. (log units)
$BeSO_4$		-0.28754	0.024669	0.026517	191	0.006091	0.002637
$MgSO_4$		-0.40878	0.055663	0.021684	178	0.002082	0.000903
$MnSO_4$		-0.49878	0.066315	0.020472	191	0.009345	0.00404
$NiSO_4$		-0.56304	0.084112	0.022191	180	0.008633	0.003733
$CuSO_4$		-0.61584	0.163894	0.003581	174	0.005886	0.002549
$ZnSO_4$		-0.54401	0.081753	0.024003	185	0.008631	0.003732
$CdSO_4$		-0.57173	0.088932	0.023283	189	0.010632	0.004593

For $\varepsilon_{II(MX)}$, almost all values are close to 0.02. The effect of ionic strength on stability of ion pairs is roughly the same for all 2-2 ion pairs. The K range is 174 – 191. This is a narrow range, possibly because the ion pairs are all sulphates. The K value for $MgSO_4$ obtained from the regression, 178, corresponds well with the value of 167 obtained experimentally by Buchner et al. (2004). De Visscher et al. (2012) proposed values around 1000 for alkaline earth carbonates based on review of literature K data. Their regression equation leads to K = 861 for $MgCO_3$, 1553 for $CaCO_3$, 646 for $SrCO_3$, and 450 for $BaCO_3$ at 25 °C. Carbonates form more stable ion pairs than sulphates.

$CuSO_4$ has a much lower solubility than the other sulphates. The molality range for $CuSO_4$ is $m = 0 – 1.4$ mol/kg. $CuSO_4$ also has the lowest K value of the sulphates.

Figure 4.7 shows the fit of the model to the literature activity coefficient data for $MgSO_4$. The fit is very good in the entire molality range.
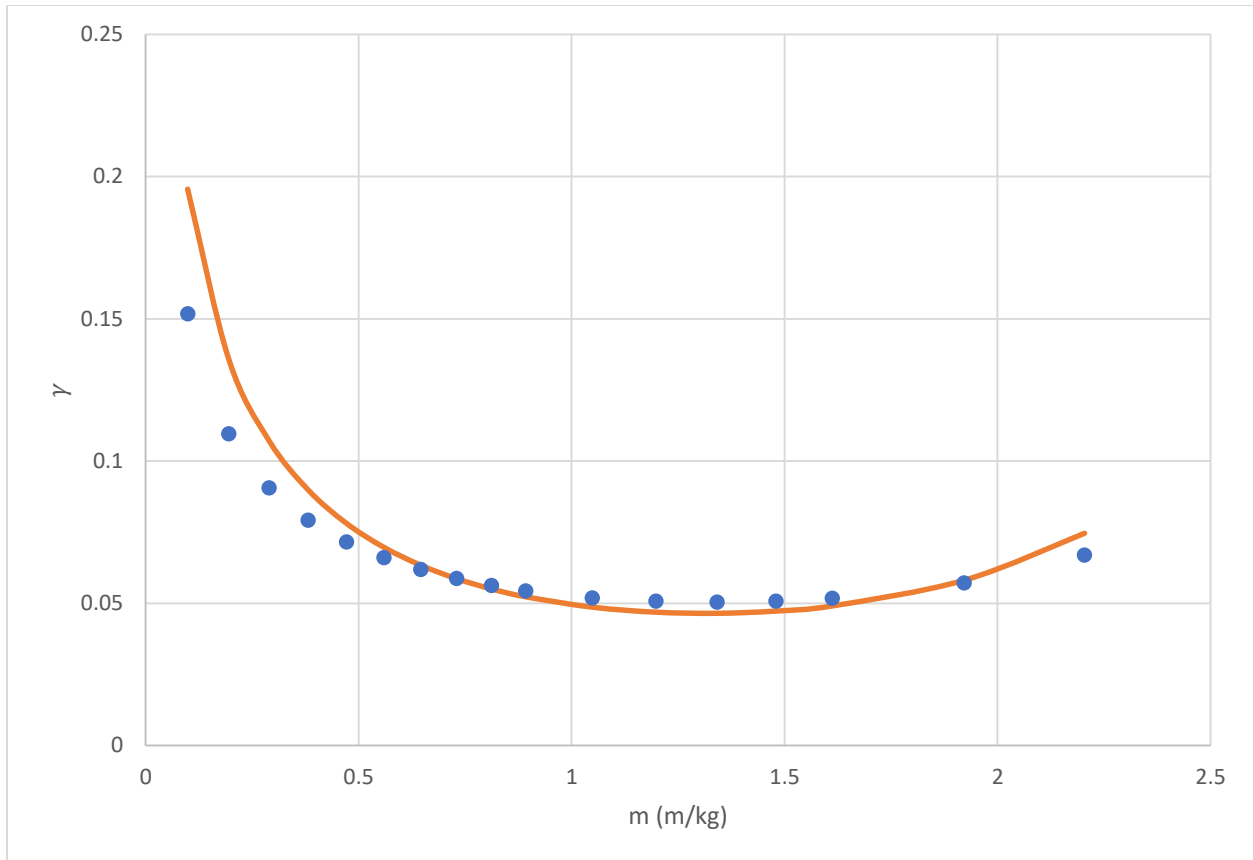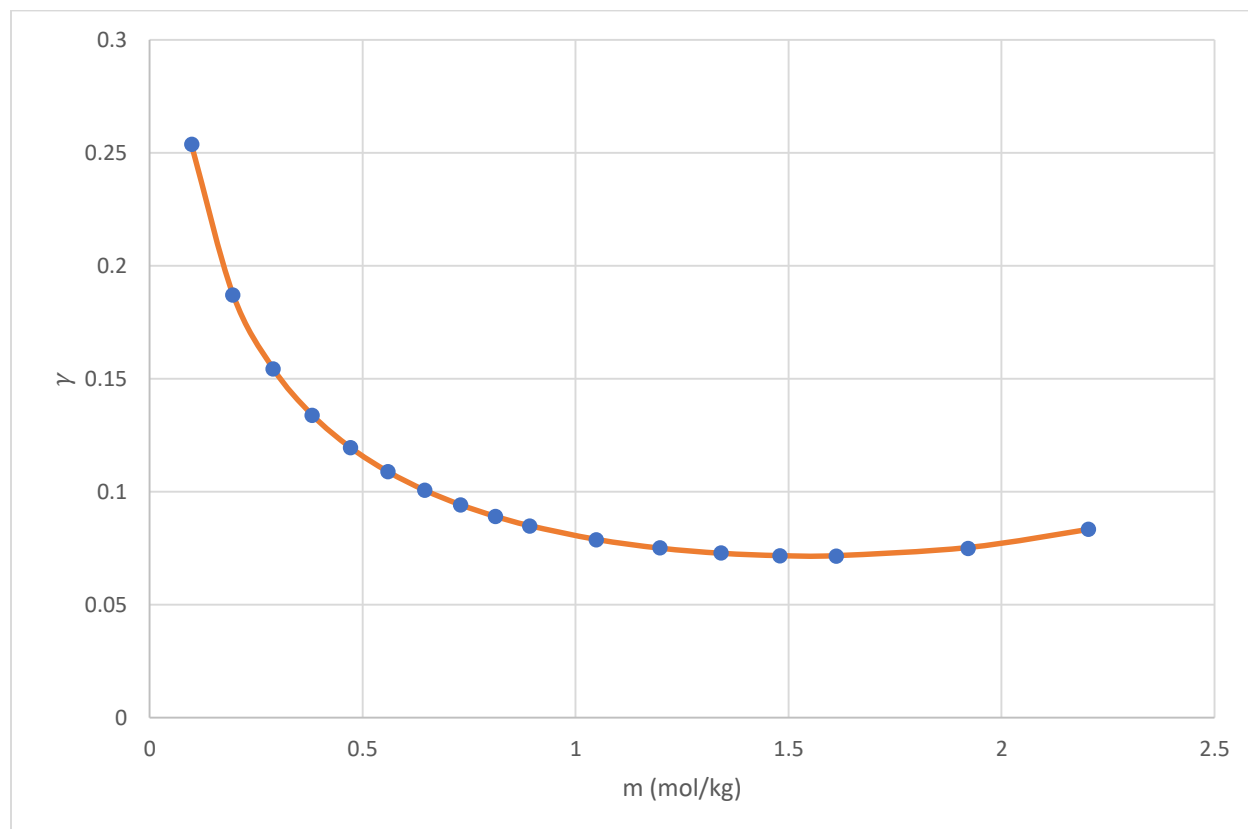

Figure 4.7 Reported activity coefficient data converted to modified molality scale (circles), and prediction with extended SIT model (line), with K, $MgSO_4$

4.5. Application of ion pairing to 1-1 electrolytes

The parameters of the extended SIT model with stability constant K were estimated by linear regression in Excel for the same electrolytes reported by Hamer and Wu (1972) as in Section 4.1. The data of HF could not be analyzed because K was so large that the free ion concentrations are very low. Instead, the data analysis was performed by forcing all the ε values to be zero. The results are shown in Table 4.5. The average standard error is 0.0034 (0.34 %), which is better than the values found without K: 0.092 (9.2 %). Without HF, in the absence of K, the remaining electrolytes were found in Section 4.1 to have a standard error of 0.013 (1.3 %). Clearly, the

inclusion of ion pairing improves the model agreement with the data, like in the case of 2-2 electrolytes.

Table 4.5 Model parameters for 1-1 electrolytes in modified molality scale. Fit to data of Hamer and Wu (1972) for m = 0-6 mol/kg; with K.

Electrolyte		ε_{MX}	ε_{MMX}	$\varepsilon_{II(MX)}$	K	Relative St. Err.	St. Err. (log units)
NaCl		0.052346	0.004344	0.038462	0.09	0.000349	0.000151
AgNO$_3$		-0.08237	0.000723	0.004494	0.45	0.002708	0.001175
HF		0	0	0	1525	0.011305	0.004882
HCl		0.139112	0.010799	0.072543	0.11	0.002807	0.001218
HBr		0.194839	0.010673	0.156495	0.09	0.002208	0.000958
HI		0.336541	0.003935	0.275595	0.17	0.011841	0.005112
HClO$_4$		0.167473	0.011996	0.190315	0.1	0.015238	0.006568
HNO$_3$		0.104576	0.000141	0.066314	0.3	0.000978	0.000425
LiOH		-0.03267	0.0408	0.019599	0.93	0.001818	0.000789
LiCl		0.114934	0.006811	0.0064019	0.07	0.001716	0.000745
LiBr		0.152073	0.011123	0.142385	0.09	0.002111	0.000916
LiI		0.32419	0.000791	0.269696	0.21	0.002385	0.001035
LiClO$_4$		0.23687	0.004813	0.188384	0.09	0.004533	0.001964
LiNO$_3$		0.103486	0.005767	0.042375	0.04	0.001101	0.000478
NaOH		0.064102	0.006368	0.041612	0.15	0.003977	0.001724
NaBr		0.0977803	0.0066859	0.0914878	0.12	0.0005061	0.0002197
NaI		0.1928322	0.0070136	0.1811477	0.24	0.0062168	0.0026915
NaClO$_4$		0.045474	0.0030496	0.582179	0.05	0.0015982	0.0006896
NaNO$_3$		0.032428	0.003032	0.012572	0.42	0.00137	0.000595
NaH2PO$_4$		-0.099007	0.0084709	0.0432582	0.1	0.0020698	0.000898
KOH		0.0873278	0.0132635	0.0684026	0.11	0.0040535	0.0017569
KCl		0.0221369	0.0021927	0.0618081	0.09	0.0043793	0.0018978
KBr		0.0609618	0.0072369	0.1064938	0.051	0.006928	0.0029984
KI		0.0616406	0.0058268	0.0403808	0.39	0.0017872	0.0007755
RbF		0.157418	0.003723	0.421168	0.01	0.000318	0.000138
NaF		0.039502	0.000992	0.014156	0.41	0.000340	0.000147
NaCNS		0.106124	0.002092	0.074438	0.08	0.001243	0.000539
KF		0.026403	0.004507	-	0	0.005001	0.002167
KNO$_3$		-0.08387	0.001057	-0.00496	0.50	0.001448	0.000629
KH2PO$_4$		-0.0316	-0.00555	0.001678	0.69	0.000623	0.000270

Figures 4.8-4.11 show the fit of the model to the literature data for the following electrolytes: NaCl, AgNO$_3$, HCl, and LiOH.
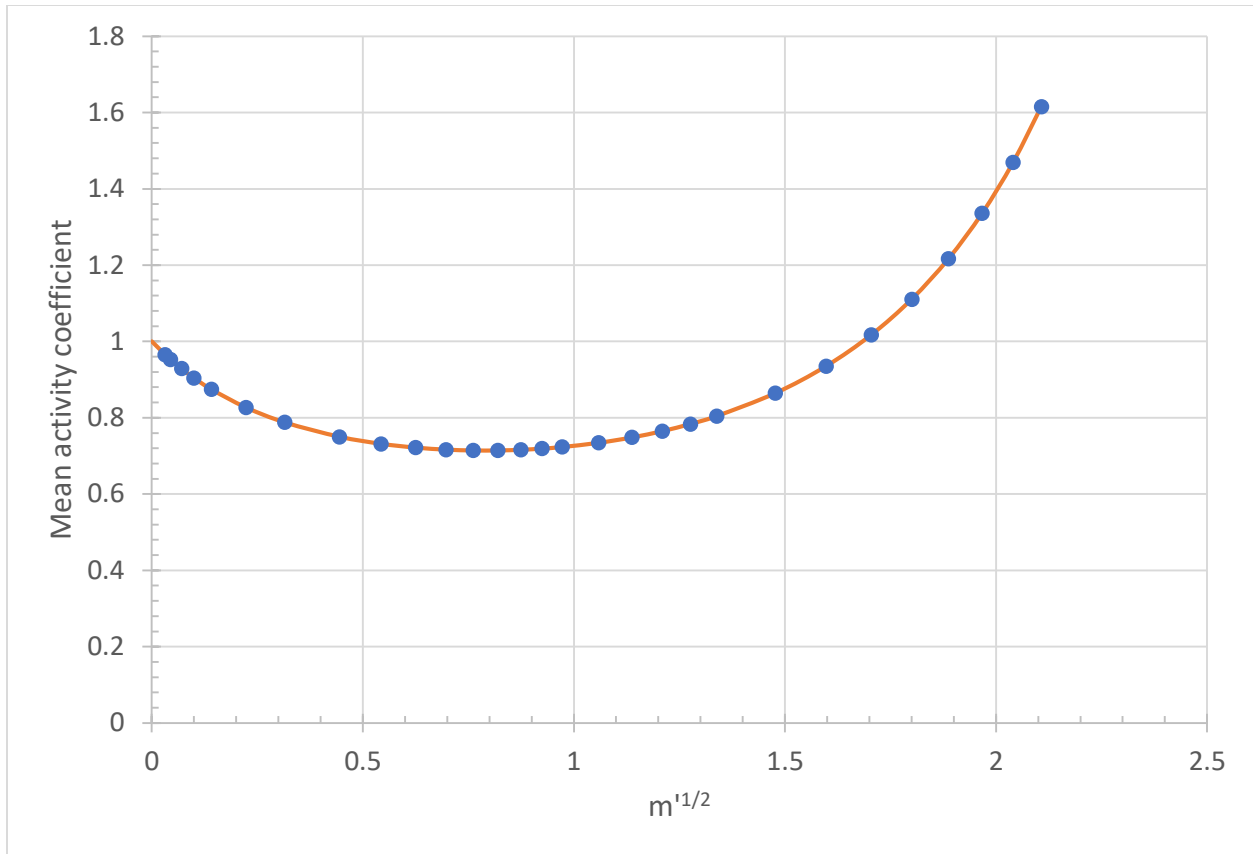
Figure 4.8 Reported activity coefficient data converted to modified molality scale (circles), and prediction with extended SIT model (line), with K, for NaCl

For NaCl, the trend is very similar to the case without K. The activity coefficient has slightly increased at high molality in the presence of ion pairing. The reason for this is that the ion pairing decreases the molality of the ions (Section 3.2.):

$$m_C = m_{C,app} - m_{CA^0} \quad (3\text{-}11)$$

$$m_A = m_{A,app} - m_{CA^0} \quad (3\text{-}12)$$

As a result, because the activity of the ions stays the same, if the molality goes down, the activity coefficient must go up:

$$\gamma_C = \frac{\gamma_{C,app} m_{C,app}}{m_C} \quad (3\text{-}14)$$

$$\gamma_A = \frac{\gamma_{A,app} m_{A,app}}{m_A} \quad (3\text{-}15)$$

Figure 4.9 Reported activity coefficient data converted to modified molality scale (circles), and prediction with extended SIT model (line), with K, for $AgNO_3$

For $AgNO_3$, introducing K improves the fit. The activity coefficient increases only slightly in spite of the fact that K is much larger for $AgNO_3$ (0.45) than for NaCl (0.09). To explain this, see the definition of K:

$$K = \frac{a_{CA^0}}{a_C \cdot a_A} = \frac{\gamma_{CA} m_{CA^0} / m^\circ}{\gamma_C m_C / m^\circ \cdot \gamma_A m_A / m^\circ} \quad (3\text{-}9)$$

Solving for m_{CA° leads to:

$$m_{CA^0} = \frac{K \cdot \gamma_C m_C \cdot \gamma_A m_A}{\gamma_{CA} m^\circ} \quad (4\text{-}1)$$
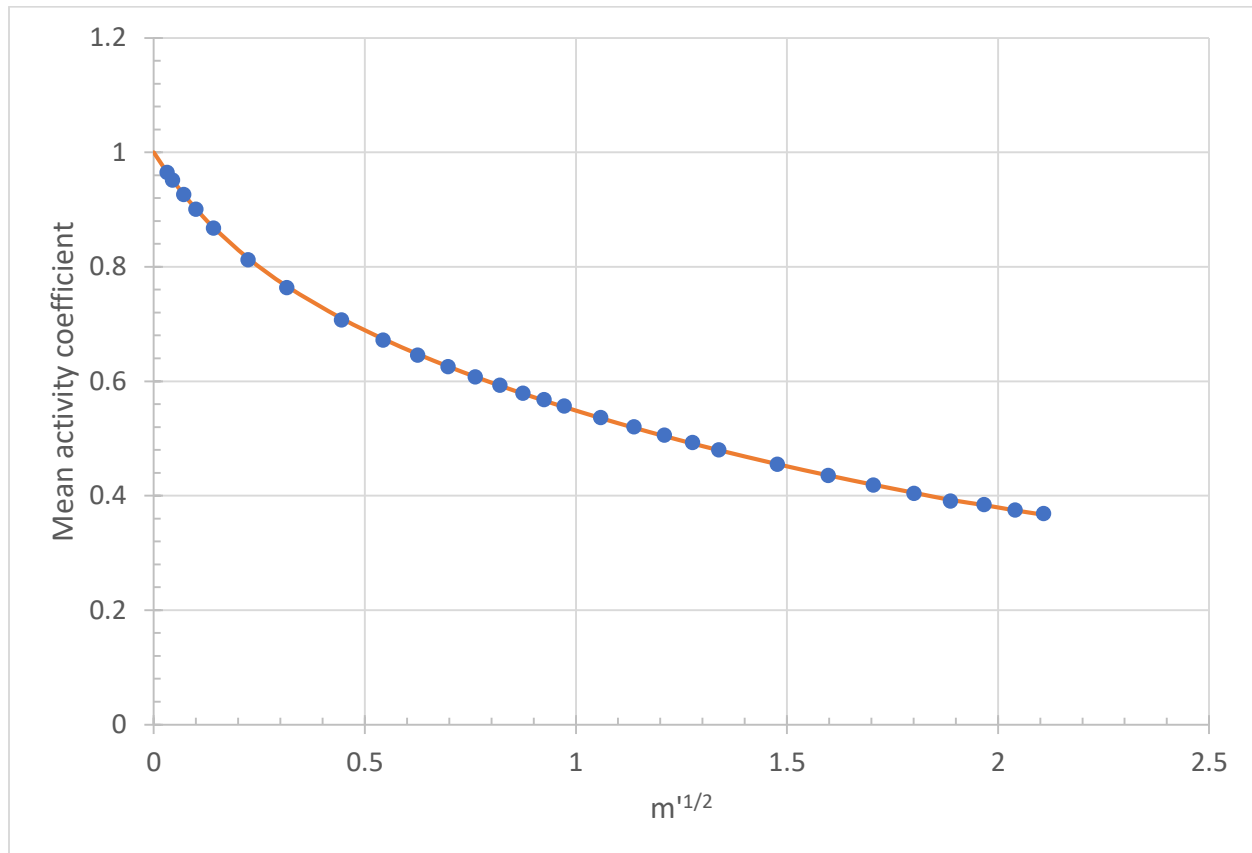

Figure 4.10 Reported activity coefficient data converted to modified molality scale (circles), and prediction with extended SIT model (line), with K, for HCl

Because γ_C and γ_A are small for $AgNO_3$, m_{CA° is also small even though K is larger than for NaCl.

The agreement between model and data has improved for HCl. The activity coefficient is much larger at high molality after introducing K, from less than 4 to more than 7. This is in spite of the fact that K is small (0.11). This is because γ_C and γ_A are large for HCl, making m_{AC° large too, as per eq. (4-1).
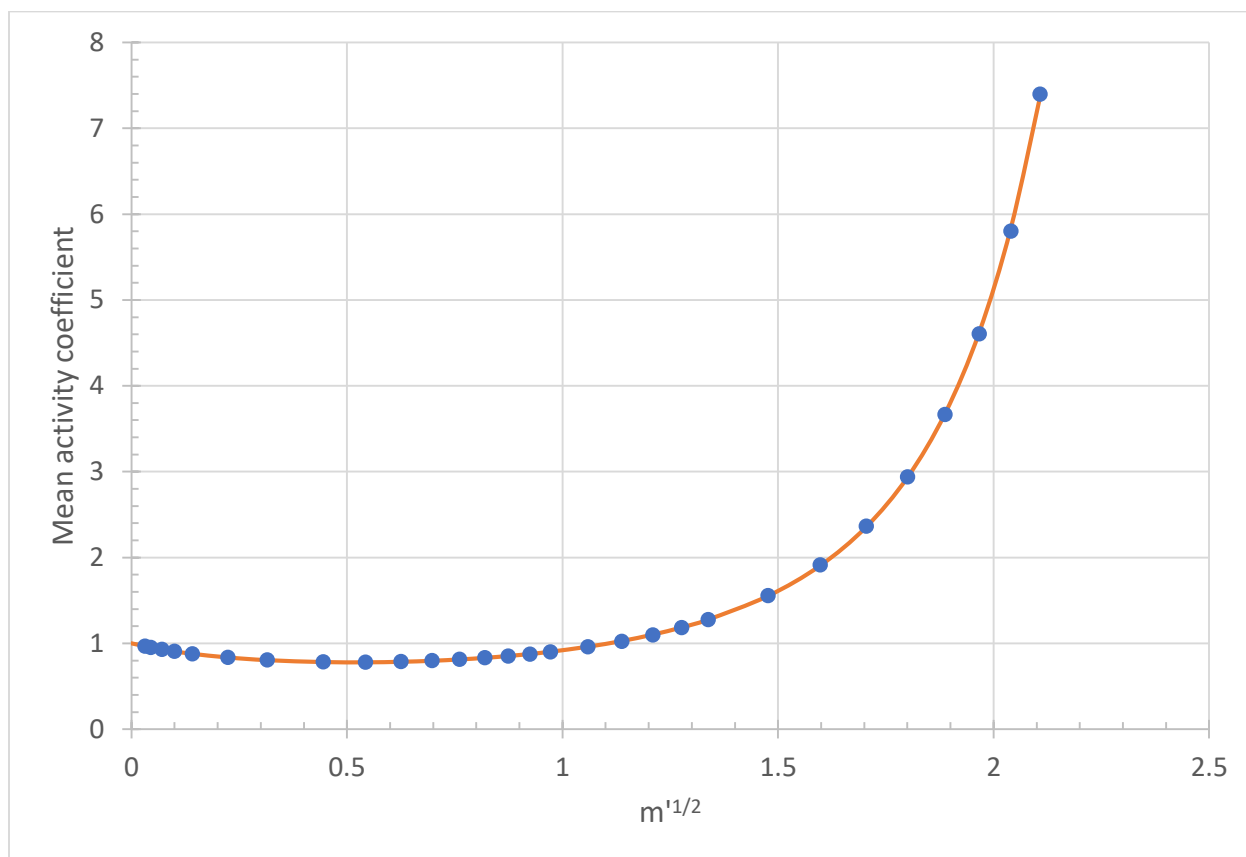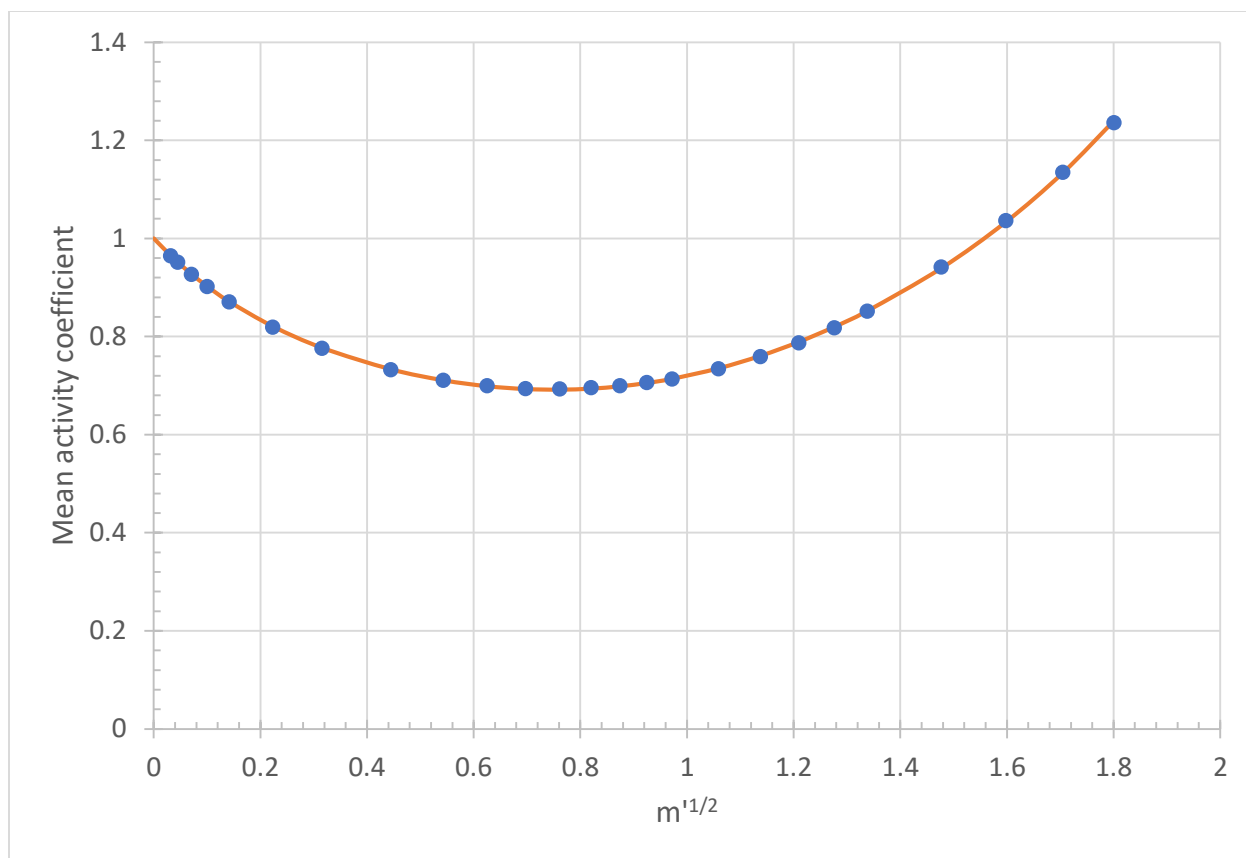
Figure 4.11 Reported activity coefficient data converted to modified molality scale (circles), and prediction with extended SIT model (line), with K, for LiOH

For LiOH, the fit between the model and the data is improved much by introducing ion pairing. K = 0.93 in this case. This time, the increase in activity coefficient is due to the large K.

4.6. Trends in ion interaction parameters

4.6.1. 1-1 electrolytes, no K

A typical observation for ion interaction parameters in other models is a regularity in the trends from H^+ to Li^+ to Na^+ to K^+. The purpose of this section is to check if this is also the case with the ESIT model. The results are shown in Table 4.6 and in Figure 4.12 for 1-1 electrolytes in the absence of ion pairing.

Table 4.6 Values of ε_{MX} for various combinations of ions

X	Cl⁻	Br⁻	I⁻	OH⁻	ClO₄⁻	NO₃⁻
M = H⁺	0.12502	0.147148	0.200535		0.01120573	0.093256
M = Li⁺	0.0977811	0.115033	0.214057	-0.083829	0.187469	0.109706
M = Na⁺	0.035089	0.059124	0.051989	0.038675	0.0399643	-0.175845
M = K ⁺	0.003522	0.053329	0.068796	0.086361		
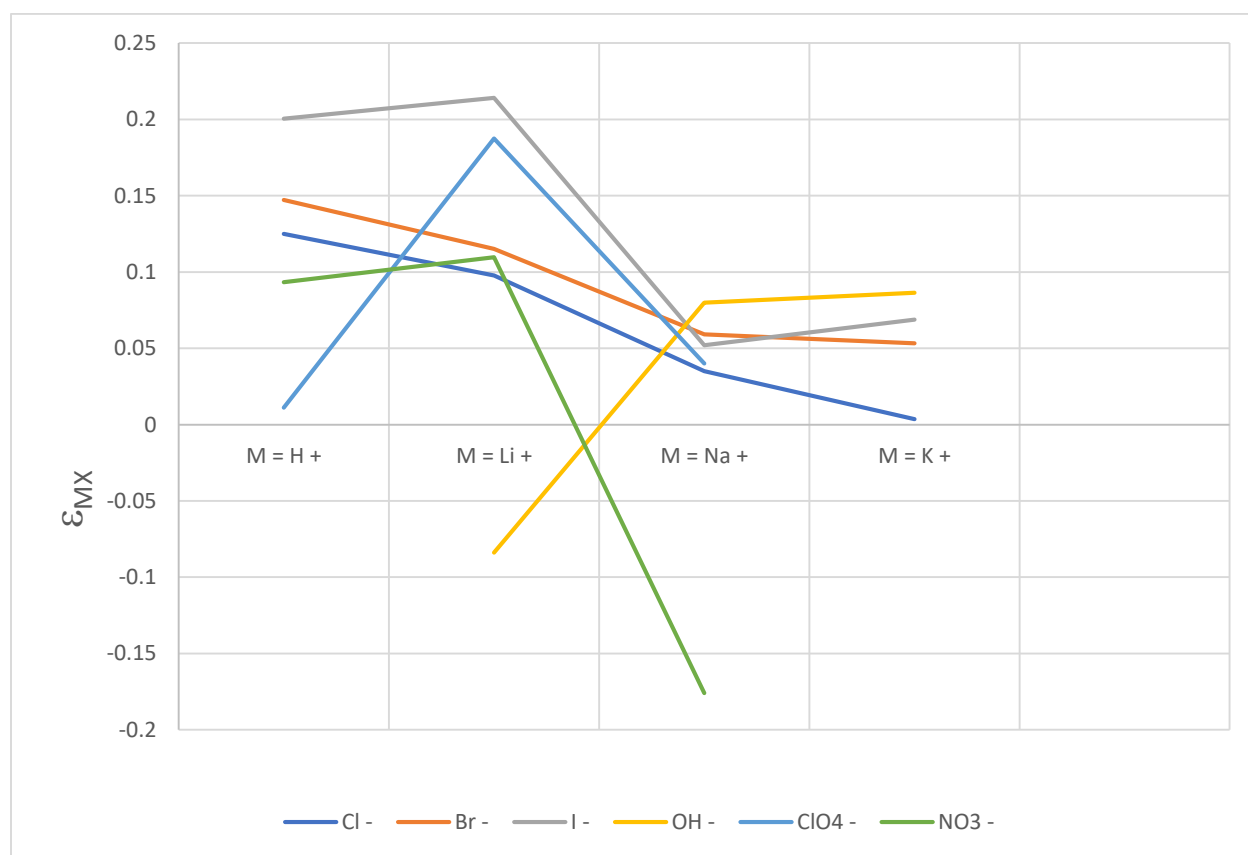
Figure 4.12 Trends in ε_{MX} for series of cations

For chloride and bromide, the values of ε_{MX} decreases from H^+ to Li^+ to Na^+ to K^+. This means, the activity coefficient $\gamma_\pm$ decreases in the same order from H^+ to K^+. This indicates that the attraction interaction between the cation and the anion increases from H^+ to K^+.

The difference between the values of ε_{MX} for chloride and bromide stay approximately the same, except for K^+ where the difference is slightly larger. For all four cations, ε_{MCl} is less than ε_{MBr}, indicating that Cl^- is more stable (less active) than Br^- in these solutions.

For the other ion combinations, the results in Figure 4.12 are more irregular. For OH^- the interaction increased from Li^+ to K^+.

Table 4.7 and Figure 4.13 show the values of ε_{MMX} for the same ion pairs.

Table 4.7 Values of ε_{MMX} for various combinations of ions

X	Cl^-	Br^-	I^-	OH^-	ClO_4^-	NO_3^-
$M = H^+$	0.003226	0.012029	0.018994		0.015622	0.001018
$M = Li^+$	0.004675	0.012045	0.010273	0.021076	0.008544	0.002187
$M = Na^+$	0.003816	0.008381	0.021418	0.011963	0.004981	0.003473
$M = K^+$	0.00393	0.007151	0.006883	0.00562		0.0066

The trends of the ε_{MMX} data are less clear than for ε_{MX}. It is proposed that this is due to a larger estimation error ε_{MMX}. However, the parameter errors estimated by the LINEST function in EXCEL both ε_{MX} and ε_{MMX} are less than 10 % in most cases. So the lack of trends is not due to parameter estimation error. It is proposed that some ion pairing occurs, which could lead to deviation of ε_{MMX}.
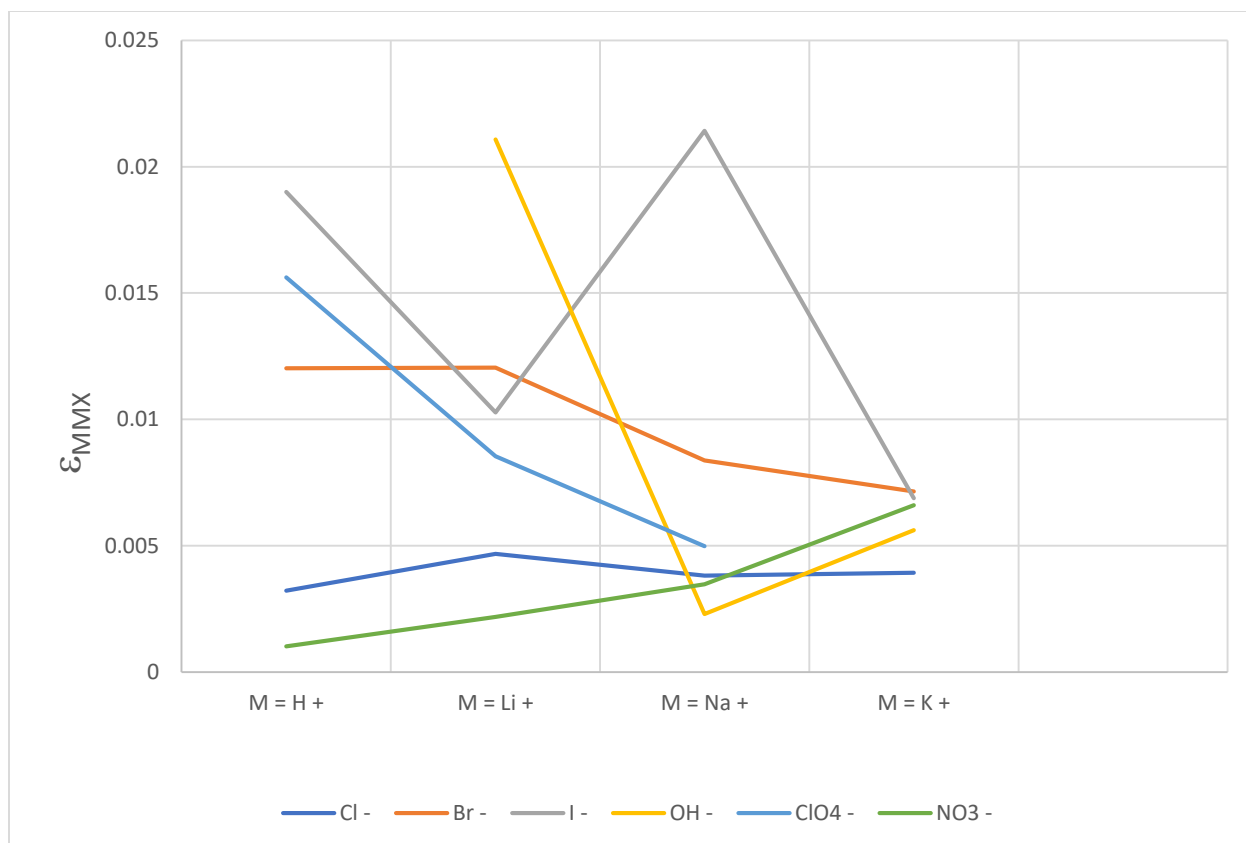
Figure 4.13 Trends in ε_{MMX} for series of cations

4.6.2. 1-1 electrolytes, with K

It was hypothesized that some of the irregularity of ε_{MX} and ε_{MMX} in Section 4.6.1 was due to the occurrence of ion pairing, and that the introduction of K would reduce the irregularities. This was tested below.

Table. 4.8. Values of ε_{MX} for various combination of ions, with ion paring

X	Cl⁻	Br⁻	I⁻	OH⁻	ClO₄⁻	NO₃⁻
M = H⁺	0.139112	0.194839	0.336541		0.167473	0.104576
M = Li⁺	0.114934	0.152073	0.32419	-0.03267	0.23687	0.103486
M = Na⁺	0.052346	0.097767	0.192832	0.064102	0.045474	0.032428
M = K ⁺	0.022137	0.060962	0.061641	0.087328		

Table. 4.9. Values of ε_{MMK} for various combination of ions, with ion paring

X	Cl⁻	Br⁻	I⁻	OH⁻	ClO₄⁻	NO₃⁻
M = H⁺	0.010799	0.010673	0.003935		0.011996	0.000141
M = Li⁺	0.0068011	0.011123	0.000791	0.04080	0.004813	0.005767
M = Na⁺	0.004344	0.006692	0.007014	0.006368	0.00305	0.003032
M = K ⁺	0.002193	0.007237	0.005827	0.013264		

Table. 4.10. Values of $\varepsilon_{II(MX)}$ for various combination of ions, with ion paring

X	Cl⁻	Br⁻	I⁻	OH⁻	ClO₄⁻	NO₃⁻
M = H⁺	0.072543	0.156495	0.27595		0.190315	0.066314
M = Li⁺	0.064019	0.142385	0.269696	0.019599	0.188385	0.042376
M = Na⁺	0.038462	0.091452	0.181148	0.041612	0.058218	0.012572
M = K ⁺	0.061808	0.106494	0.040381	0.068403		

Table. 4.11. Values of K for various combination of ions, with ion paring

X	Cl⁻	Br⁻	I⁻	OH⁻	ClO₄⁻	NO₃⁻
M = H⁺	0.11	0.09	0.17		0.10	0.03
M = Li⁺	0.07	0.09	0.21	0.93	0.09	0.04
M = Na⁺	0.09	0.12	0.24	0.15	0.05	0.42
M = K ⁺	0.09	0.051	0.39	0.11		

Tables 4.8-4.11 show the values of ε_{MX}, ε_{MMX}, $\varepsilon_{II(MX)}$, and K for the same ion pairs as the previous section. The trends in ε_{MX} are shown in Figure 4.14. The figure shows more regular results for I⁻ and NO₃⁻. However, for ClO₄⁻, the results remain irregular.

Figure 4.15 shows the trends for ε_{MMX}. The results remain irregular. Due to the high value of ε_{MMX} for LiOH, the trend is even more irregular for the hydroxides. This is linked to the very high value of K for LiOH (0.93, one of the largest for all 1-1 electrolytes).

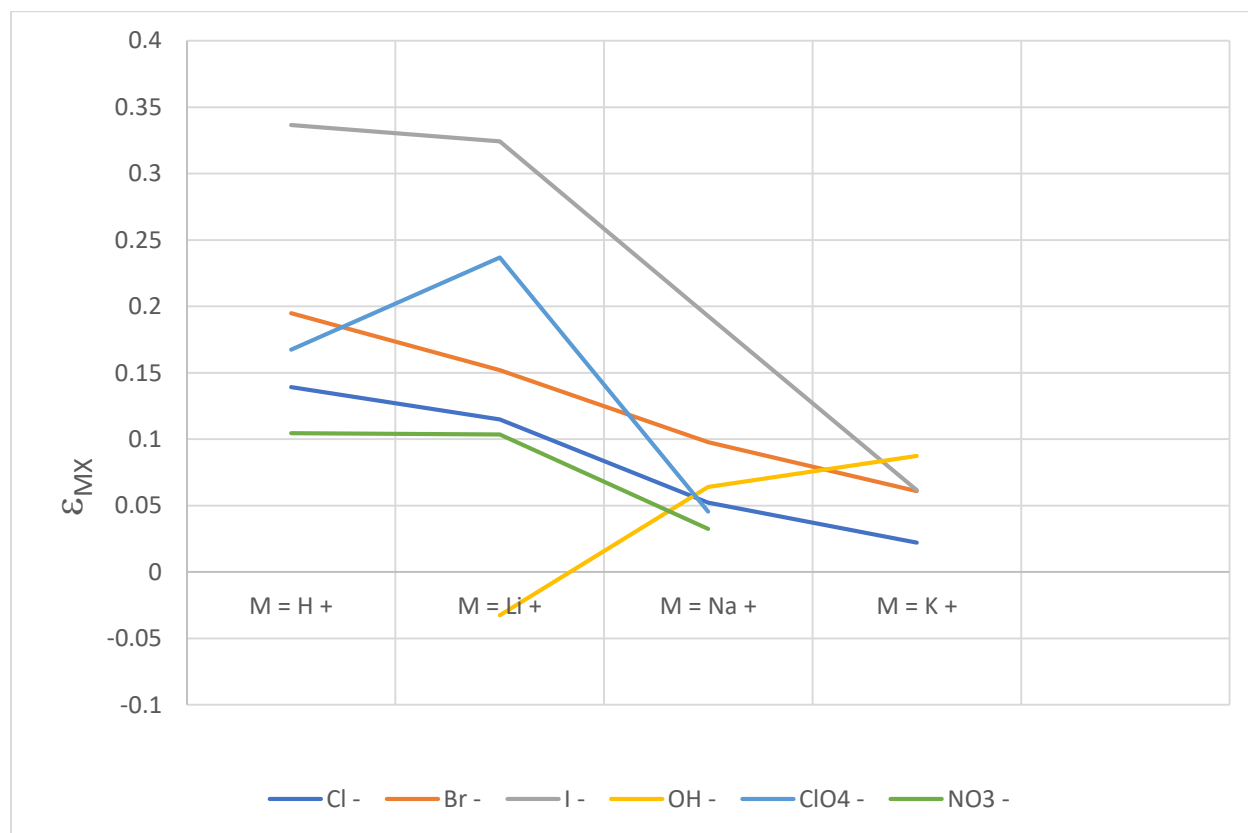Figures for $\varepsilon_{II(MX)}$ and K are not shown because no clear trends were observed.

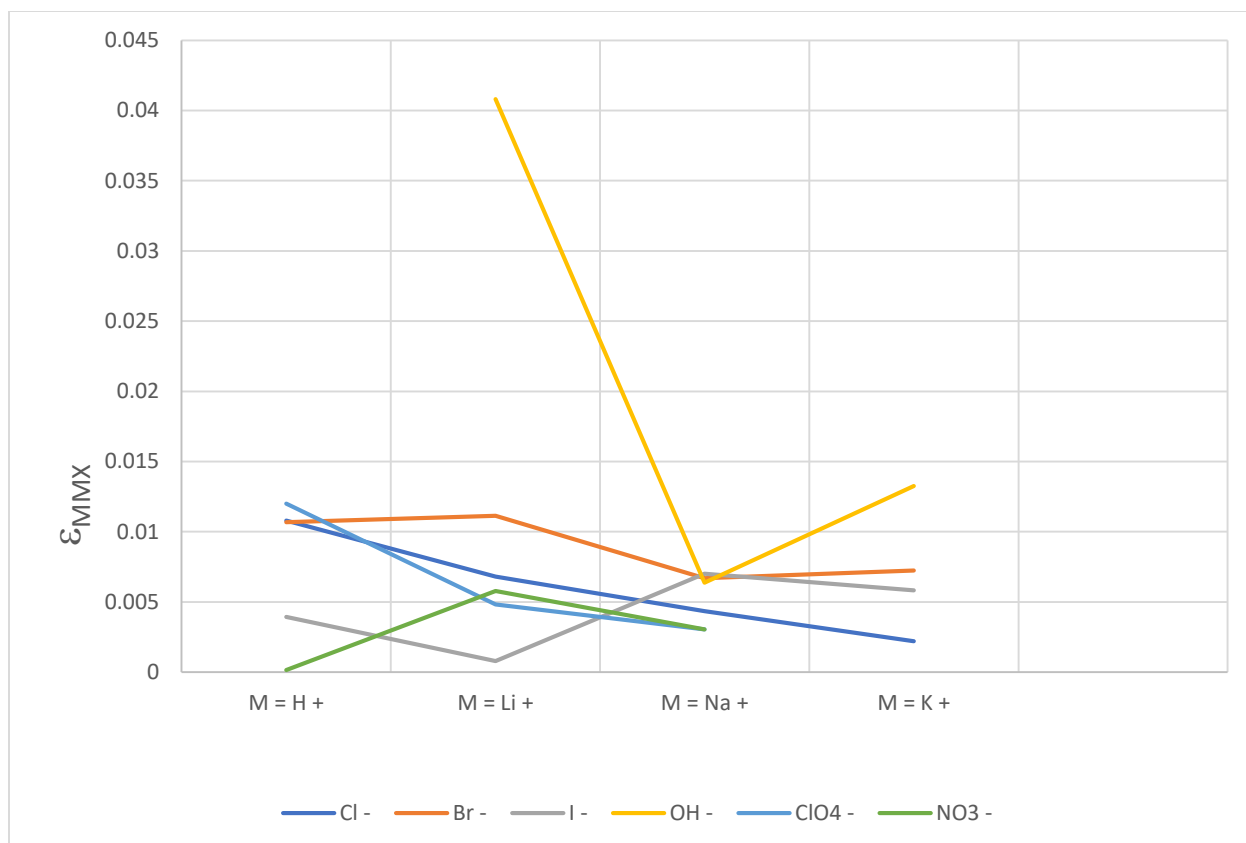Figure 4.14 Trends in ε_{MX} for series of cations, with K

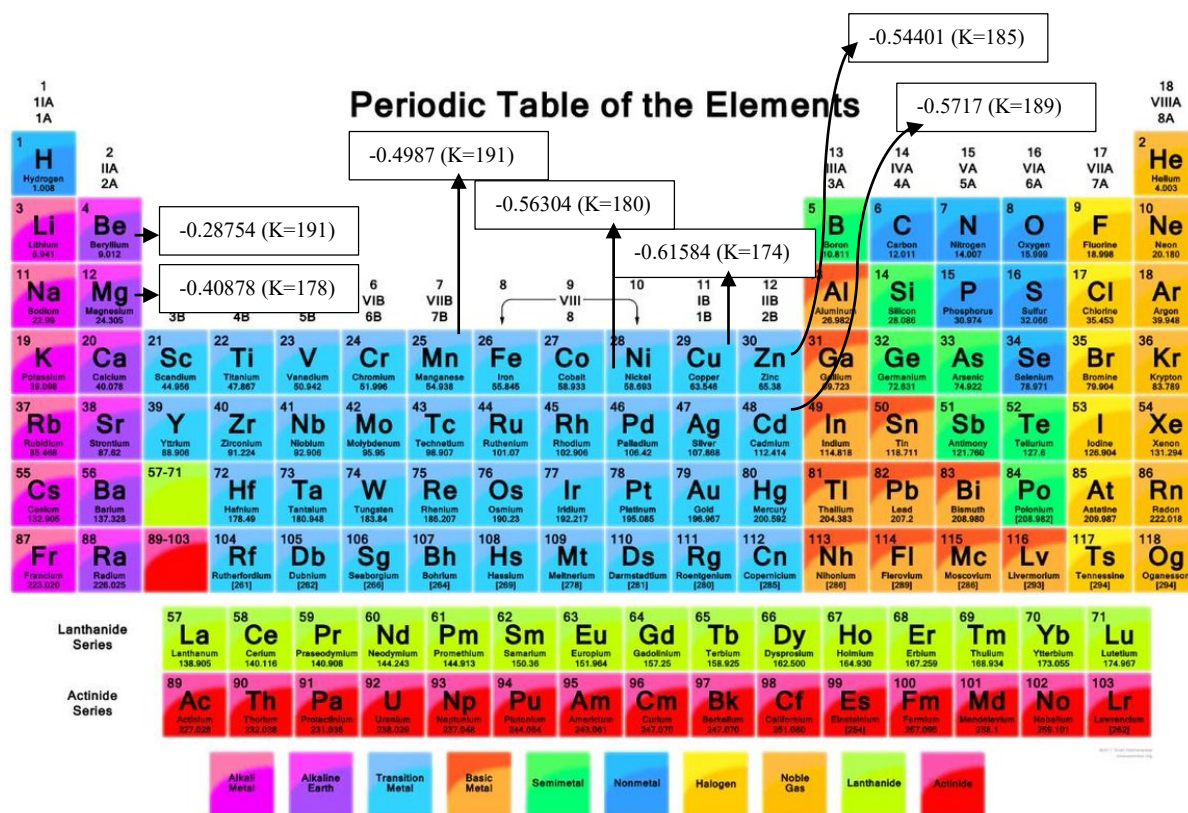Figure 4.15 Trends in ε_{MMX} for series of cations, with K

4.6.3. 2-2 electrolytes, with K

Table 4.12 contains data for only two alkaline earth sulphates, $BeSO_4$ and $CaSO_4$ so only limited conclusions can be drawn. ε_{MX} decreases from -0.2875 for Be^{2+} to -0.4088 for Mg^{2+}. They are elements of the second group of the periodic table whose electron configuration ends with ns^2, where n is the row number, meaning that the valence electrons are two electrons in orbital ns. These electrons are the ones removed to form the ion M^{2+}. These metals have a shiny surface and silver-white color. They have high reactivity. But the reactivity of this group is not as high as alkali metals (group I). A decrease of ε_{MX} going down the periodic table was also seen for the alkaline metal salts of chlorine and bromine.

Table 4.12 also contains data for four metals in row 4 of the periodic table: Mn^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. These are transition elements. They are all metallic in nature. In terms of position in the periodic table from the third group onwards, transition elements are located in ten groups. In terms of electron arrangement, unlike alkali and alkaline earth metals of the same period, the

energy level of the (n-1) d level of their valence layer is lower than the ns level of this layer. Therefore, the last electron of their atom enters in (n-1) d and the level of the valence p layer and their atom is empty of electrons.

Tabel.4.12. ε_{MX} and K of sulphates of various bivalent metals in the periodic table

-0.54401 (K=185)

-0.5717 (K=189)

-0.4987 (K=191)

-0.56304 (K=180)

-0.28754 (K=191)

-0.61584 (K=174)

-0.40878 (K=178)

According to the periodic table, the value of K is variable. In the second column of the table, which are alkaline earth metals, the value of K is decreasing from top to bottom. For the transition metals, no clear trend of K can be observed. The value of K in this row (group 4) is decreasing intermittently, except for copper.

From the table, it can be seen that alkaline earth metals have less negative ε_{MX} than transition metals, whereas K is similar for the two types of metals.

4.7. Effect of ion pairing on ionic strength and Debye-Huckel term – 2-2 electrolytes

The Debye-Huckel term is the electrostatic contribution to the activity coefficient of electrolytes. In the SIT and ESIT model, it is expressed by:

$$\log \gamma_{DH} = -\frac{A z_i^2 \sqrt{I}}{1 + 1.5\sqrt{I}} \quad (4\text{-}1)$$

where A = 0.51 at 25 °C. The ionic strength is given by:

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (1\text{-}1)$$

In the case of a single 2-2 electrolyte, this simplifies to:

$$I = 4m \quad (4\text{-}2)$$

where m is the molality of the electrolyte. However, this assumes that all ions in the solution are free ions. However, it was shown that a fraction of the ions form ion pairs and do not contribute to the ionic strength. Therefore, the ionic strength in a model accounting for ion pairing is less than the ionic strength in a model without ion pairing. This will also affect the Debye-Huckel term in the activity coefficient.

Figure 4.16 shows the ionic strength of a $MgSO_4$ solution as a function of the modified molality, for the model without ion pairing and the model with ion pairing. Without ion pairing, the relationship is a straight line based on eq. (4-2). With ion pairing, the ionic strength is less, and the relationship is not linear. The difference between the ionic strengths calculated by the two models is about 40 % at low molality, and about 20 % near saturation. Similar numbers were found for the other 2-2 electrolytes.
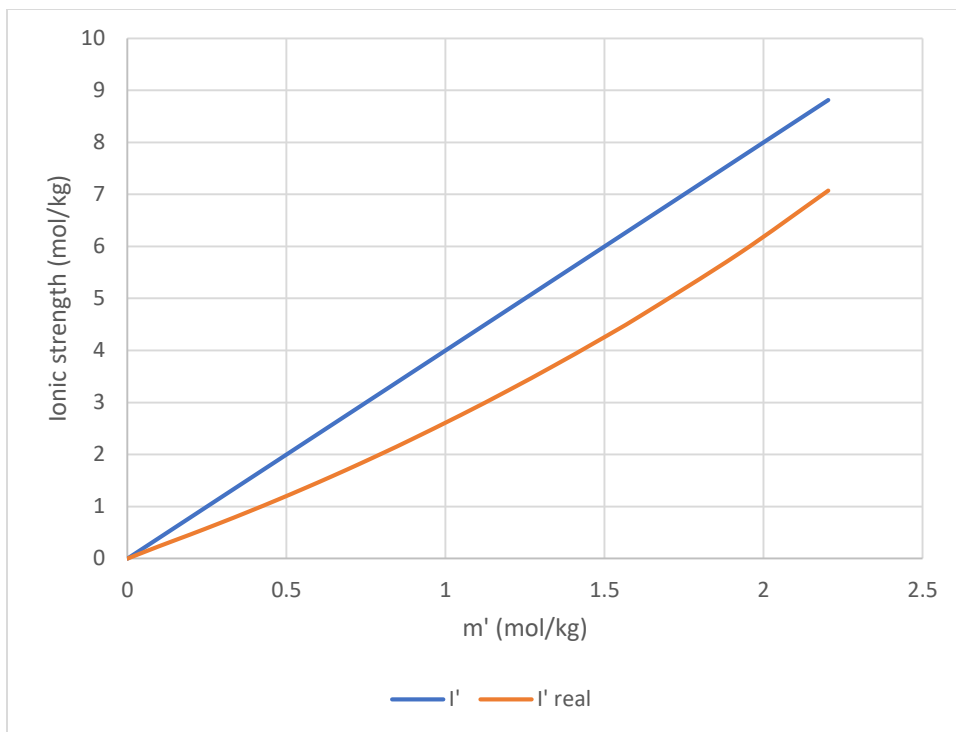
Figure 4.16. Ionic strength of $MgSO_4$ as a function of modified molality in the absence of ion pairing (blue line) and in the presence of ion pairing (orange line)

Figure 4.17. shows the Debye-Huckel term in log scale as a function of modified molality. The difference between the model with ion pairing and the model without ion pairing is about 0.09 log units at low molality, and about 0.02 log units at saturation. This means that the Debye-Huckel contribution to the activity coefficient in linear scale is about 23 % higher in the presence of ion pairing, than is predicted by a model without ion pairing at low molality. At saturation, the difference is about 5 %.

In a model without ion pairing, the Debye-Huckel term is underestimated, and this is compensated by the specific ion interaction terms. As a result, the specific ion interactions are overestimated in models without ion pairing. Adding ion pairing to the model makes the description of the interactions more realistic.
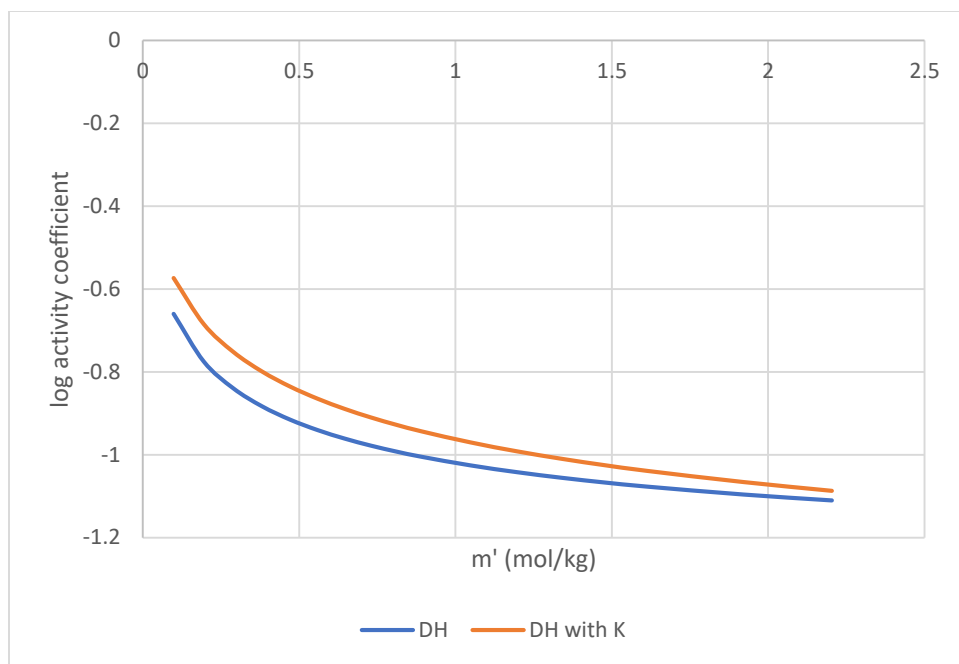
Figure.4.17. Debye-Huckel term in log scale for MgSO$_4$ as a function of modified molality in the model without ion pairing (blue line) and in the model with ion pairing (orange line)

4.8. Potential applications of the extended SIT model with ion pairing

Areas where ion activity coefficients are needed are chemistry and pollution of natural waters and geochemistry. Ions such are Mg^{2+} and SO$_4^{2-}$ are abundant in the environment. Another area where the model could be beneficial is in some industrial processes, such as scaling in boilers and desalination. An area where accurate activity coefficient models in complex systems are important is in the storage of nuclear wastes, where the solubility of radionuclides determines the safety of the storage method.

Chapter 5. Conclusions and Recommendations

A fairly straightforward model for describing the activity coefficients of ions in electrolyte solutions is the specific ion theory (SIT). Ion pairing, a prominent occurrence in 2-2 electrolytes, is not included by the SIT model in its original form. This thesis expands on a recent SIT model extension to take ion pairing into consideration. Using literature data for $BeSO_4$, $MgSO_4$, $MnSO_4$, $NiSO_4$, $CuSO_4$, $ZnSO_4$, and $CdSO_4$, the model extension is put to the test. The model's standard error is normally 1% or less. Without accounting for ion pairing, the model's standard error is about 10 %. The predicted values of the ion pairing equilibrium constant, K, range from 174 to 191. The value for $MgSO_4$, 178, corresponds well with the value obtained experimentally by Buchner et al. (2004), which is 167.

It is determined that failing to take into consideration ion pairing causes up to 30% overestimations of ionic strength and up to 20% overestimations of the Debye-Huckel term for the activity coefficient of 2-2 electrolytes.

Introducing ion paring also improved the model fit for 1-1 electrolytes. Without ion pairing, the standard error of the model is 1.3 %. After introducing ion pairing, the standard error is 0.34 %. For 1-2 electrolytes, the standard error of the model is 1.38 % in the absence of ion pairing, similar to 1-1 electrolytes. It is expected that introducing ion pairing will improve the model performance for 1-2 electrolytes as well.

For future research, it is recommended to extend the study to more electrolytes, including 1-3 electrolytes, and to introduce ion pairing to 1-2 and 1-3 electrolytes. It is also recommended to extend the analysis to temperatures other than 25 °C, for electrolytes where such data is available in the literature.

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