THERMODYNAMICS

OF

AQUEOUS ELECTROLYTE SOLUTIONS

BY

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TO MY FAMILY

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ABSTRACT

The focus of this work is the thermodynamics of aqueous solutions of strong electrolytes for both binary and multicomponent systems.

A new excess Gibbs energy function to represent the deviations from ideality of binary electrolyte solutions was derived. The function consists of two contributions, one due to long-range forces, represented by the Debye-Hückel theory, and the other due to short-range forces represented by the local composition concept. The model is valid for the whole range of electrolyte concentrations, from dilute solutions up to saturation. The model consistently produces better results particularly at the higher concentration regions in which the other models deteriorate.

An electrochemical cell apparatus using Ion-Selective Electrodes (ISE) was constructed to measure the electromotive force (emf) of ions in the aqueous electrolyte mixtures. For the NaCl-NaNO₃-H₂O system, the data for the mean ionic activity coefficient of NaCl was obtained in order to show the reproducibility of literature data and to test the validity of the experimental procedure. The data for mean ionic activity coefficient of the following systems were also collected.

- 1. NaBr-NaNO₃-H₂O (a system with common ion)
- 2. NaBr-Ca(NO₃)₂-H₂O (a system with no-common-ion)

A novel mixing rule was proposed for the mean activity coefficients of electrolytes in mixtures in terms of the mean ionic activity coefficients of electrolytes in the binary solutions. The rule is applicable to multicomponent systems which obey Harned's Rule. Predictions are in excellent agreement with experimental data for ternary systems which follow the Brönsted specific ionic theory.

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RESUME

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L'object principal de ce travail est l'étude thermodynamique des solutions aqueuses des électrolytes fortes pour des systèmes binaires et à composés multiples.

Une nouvelle fonction d'énergie d'excés de Gibbs représentant les déviations de l'idéalité des solutions électrolytiques binaires a été introduite. Dans cette fonction interviennent deux termes, le premier est dû aux forces à longue distance représentées par la théorie Debye-Hückel et le second est relié aux forces à courte distance représentées par le concept de composition locale. Le modèle est applicable aussi bien aux solutions diluées qu'aux solutions saturées. Les résultats obtenus sont meilleurs que ceux obtenus par d'autres modèles surtout dans le cas des concentrations élevées.

Une cellule électrochimique utilisant des électrodes à ions sélectifs (EIS) a été construite à fin de mesurer la force électromotrice (fem) des ions dans les mélanges électrolytiques aqueux. Pour le système NaCl-NaNO₃-H₂O, le coefficient moyen d'activité ionique de NaCl a été calculé pour reproduire les données de la littérature et démontrer ainsi la validité de la procédure expérimentale. Dans cette étude des données ont été tabulées pour les systèmes suivants:

- 1. NaBr-NaNO₃-H₂O (un système avec un ion en commun)
- 2. NaBr Ca(NO₃)₂-H₂O (un système sans ion en commun)

Une nouvelle règle des mélanges a été proposée pour déterminer le coéfficient d'activité moyen des mélanges d'électrolytes. Cette règle est décrite en termes des coéfficients d'activité moyen des solutions électrolytiques binaires. Elle est applicable aux systèmes multicomposés obéissant à la règle d'Harned. Les prédictions sont en trés bon accord avec les résultats expérimentaux pour les systèmes ternaires qui obéissent à la théorie d'ions spécifique de Brönsted.

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NOMENCLATURE

Upper Case Letters

Α	Anion
A	Debye-Hückel universal constant
B	Debye-Hückel parameter
$B_{ca'},$	$B_{ac'}$ Guggenheim's parameters
B	Bromley's parameter
С	Cation
C_p	Heat capacity
D	Dielectric constant
E	Potential of electrochemical cell
F	Faraday constant, 96485 coulombs/mole
G	Gibbs energy
H_f^o	Heat of fusion
Ĺ	Ionic strength
I,	Ionic strength of salt i
I(i)	Ionic Strength of ion i
K_{ij}^{pot}	Selectivity coefficient, selective to ion i towards ion j
M	Molecular Weight of solvent
Ν	Number of experimental data points
N^o	Avogadro's number, 6.02252 x 10 ²³ J.K
Р	Pressure
R	Universal gas constant
R	Isopiestic ratio
S	Entropy
S	Salt
S	Slope of electrode
Т	Temperature
U	Mobility
V	Volume
W	Water
X	Effective mole fraction
X_{ij}	Effective local composition of species i around species j
Y_{i}	Ionic strength fraction of electrolyte i
Y(i)	Ionic strength fraction of ion i
Ζ	Coordination number
Z^+	Charge number of cation
Z-	Charge number of anion

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Lower Case Letters

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a	activity
a	distance of closest approach
с	molarity, mole/l
с	direct correlation function
е	electric charge, $1.6021 \ge 10^{-19} \text{ C}$
f	fugacity
g	radial distribution function
g^{ex}	molar excess Gibbs energy
g_i^{ex}	molar excess Gibbs energy of species i
g_{ij}	interaction energy between two species i and j
g_1^o	reference excess Gibbs energy of species i
h	total correlation function
k	Boltzmann constant, $1.38054 \ge 10^{-23} \text{ J.K}$
m	molality
n	number of moles
r	intermolecular or interionic distance
\overline{v}	partial molar volume
x	mole fraction
x_{ij}	local composition of species i around species j

Greek letters

$lpha_{12}, lpha_{12}'$	Harned's coefficient of salt 1, $\alpha'_{12} = \alpha_{12} \ln(10)$
eta_E	electrolyte interaction energy parameter
β_W	solvent interaction energy parameter
$oldsymbol{eta}$	Debye-Hückel parameter
$\gamma(i)$	activity coefficient of component i
γ_{*}	activity coefficient of species i
γ_{\pm}	mean ionic activity coefficient
Γ	Meissner reduced activity coefficient
Γ.,	Non-random factor of species i around species j
κ	reciprocal thickness of the ionic atmosphere
λ	NRTL-NRF parameter
$\lambda_{ij}(I)$	Pitzer parameters
λ_E	electrolyte adjustable parameter
λ_W	solvent adjustable parameter
μ	chemical potential
μ_{ijk}	Pitzer parameters
ν	stochiometric number of electrolyte
ν+	stochiometric number of cation
ν-	stochiometric number of anion

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 $\begin{array}{lll} \rho & \mbox{density} \\ \sigma & \mbox{closest distance approach} \\ \sigma_{\gamma} & \mbox{root mean square deviation of logarithm values} \\ \tau & \mbox{local composition parameter} \\ \phi^{\rm t} & \mbox{potential of ion in phase i} \\ \phi & \mbox{practical osmotic coefficient} \\ \psi & \mbox{intermolecular or interionic potential} \end{array}$

Superscripts

+	cation
	anion
0	measurements in binary electrolyte solution
θ	standard state
*	mole fraction standard state
α	phase α
eta	phase β
∞	infinite dilution
el	electric
sp	solubility product
tr	trace
ex	excess
(x)	mole fraction standard state
(m)	molality standard state
(c)	molarity standard state

Subscripts

+	cation
-	anion
±	mean
i, j, k	component or species
A	ani^n
С	cation
D	double junction electrode
E	electrolyte
W	water
R	reference
S	single junction electrode
S	salt
8	solvent
r	mole fraction
DH	Debye-Hückel
NRTL – NRF	Non-Random Two Liquid-Non-Random Factor

- experimental exp calc
- calculated
- ASY asymmetry

Special Symbols

- natural logarithm with base "e" ln
- log logarithm with base 10
- д sign for partial derivative

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Chapter 1

Introduction

1.1 General

Aqueous electrolyte solutions play an important role in chemical, biological and environmental systems Electrolyte solutions are distinct and different from nonelectrolyte solutions. The presence of both ionic and molecular species in solution is one of the most important aspects differentiating electrolyte systems from nonelectrolyte mixtures. According to the Arrhenius [7,8,9] theory, electrolytes partially dissociate in a solvent with the extent of dissociation depending on the dielectric properties of the solvent. Based on the degree of dissociation, aqueous electrolyte solutions can be classified into three groups. The first group is made up of strong electrolytes such as NaCl and KOH, which nearly completely dissociate to charged ions when dissolved in water. The second type is that of complex electrolytes such as H_3PO_4 and H_2SO_4 which form ionic or molecular intermediates in aqueous solutions. The final group consists of weak electrolytes, such as CO_2 and H_2S , which form a subset of complex electrolytes with water.

As a consequence of the presence of both ions and molecular species in electrolyte systems, both chemical and physical equilibria are present simultaneously. A wide variety of chemical reactions can occur in multicomponent electrolyte mixtures leading to complex solution chemistry. The study of liquid (aqueous) phase equilibria in systems such as those found in distillation using salts as additional separation agents

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or in sour water stripping are specific cases in which the solution chemistry involves both chemical and physical equilibria. Other examples of this type of chemistry are found in studies of liquid (organic)-liquid (aqueous) phase equilibria of hydrocarbon sour water systems or in studies of liquid-liquid extraction of aqueous solutions of metals.

One important aspect of electrolyte systems, which particularly concerns our research, is the strong thermodynamic non-ideality of the liquid phases. This is due to interionic and intermolecular interactions among the various ionic and molecular species. The presence of long-range interionic forces in mixtures containing electrolytes results in high deviations from thermodynamic behavior of the ideal solutions. A theoretical study of the thermodynamic properties of electrolyte systems should consider the contributions of at least two effects, one related to long range coulombic forces between ions and the other short range Van der Waals type forces between the species. The short range effects are particularly important at high concentrated electrolyte solutions. These two forces will be discussed in Chapter 3

The study of electrolyte systems, particularly of aqueous electrolyte solutions, has a wide diversity of applications in chemical, environmental, and biological industries. In an academic sense one can classify the applications of electrolyte systems according to the physical equilibria involved, *i.e.*, Vapor-Liquid Equilibria (VLE), Liquid-Liquid Equilibria (LLE) and Liquid-Solid equilibria (LSE). For instance, NaOH scrubbing technology for the removal of sulfur compounds and carbon dioxide from process gas streams is one case of VLE which is important in preventing acid rain problems. Similarly the study of the vapor-liquid equilibria of the NH₃ CO₂ H₂O systems is industrially important for accurate design of sour-water strippers

Most recently, interest has been focused on the effects of electrolytes in two liquid phase systems used in biological separations. It has been found that inorganic salts such as Na_2SO_4 , $MgSO_4$, K_3PO_4 and even certain uni-univalent salts such as NaClare important in the formation of such two-phase aqueous systems [3,29]. The main advantage of this technique is the use of two aqueous phases making it possible to control the partitioning of biological substances between the two phases. It has been also observed that electrolytes have an important effect in separation of organelles, enzymes, proteins and other substances, from biological mixtures using membranes or gels.

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Liquid Solid equilibria systems involving electrolytes are to be found in the following processes: sea water desalination, corrosion, crystallization processes in geological systems (geothermal brines or drilling muds), ion exchange, hydrometallurgy of ores, electro-metallurgical extraction and refining of metals. The list of industrial problems which would benefit from a better understanding of electrolyte solutions is virtually endless. We have quoted a few examples here for the purpose of showing the variety of fields in which the effect of electrolytes is important.

1.2 Thermodynamic Properties of Electrolyte Solutions

The current state of the thermodynamic knowledge of aqueous electrolyte solutions is the result of the almost one century of research. Among the thermodynamic properties of aqueous electrolyte solutions, the Gibbs free energy and related functions such as heats of mixing, mean activity coefficient or osmotic coefficient are particularly important. Other properties such as the equilibrium constants of reactions and heat capacities are also of some interest. These thermodynamic properties are useful in process design. For example, data on the vapor-liquid equilibria of the $Mg(NO_3)_2$ - $HNO_3 \cdot H_2O$ systems are necessary for column design in the extractive separation of nitric acid. In this process, the HNO_3 -H₂O azeotrope can be broken by adding $Mg(NO_3)_2$ salt to the liquid solution [124]. This type of phenomenon is referred to as salting-in and salting-out effects in distillation operations [49,51,52]. Furter has presented excellent reviews of the effects of salts in distillation [50,53]. In the thermodynamic modelling of gels, used in separation of biological compounds, one needs a knowledge of the osmotic coefficients in order to estimate the effect of osmotic pressure in the swelling behavior of the gels [129].

Experimental thermodynamic studies of aqueous solutions of electrolytes involve measurements of mean activity coefficients of the electrolytes and the osmotic coefficient of the solvent. In relation to this thesis it is interesting to mention that almost all experimental data in literature belong to single salt aqueous mixtures or to ternary electrolyte solutions containing two salts with a common ion [63,64,116]. In addition, most of the experimental data collected on ternary systems are activity or osmotic pressure of the solvent. Individual measurements of the mean activity coefficients of salts are rarely reported. For example, the mean ionic activity coefficients of NaCl and KCl with common anion [23] or NaNO₃ and NaCl with common cation [83] have been reported but, to the best of this author's knowledge, the measurements of activity coefficients for KCl and $NaNO_3$ (without a common ion) have not been reported and only the osmotic coefficient of water has been measured for this system [12]. Experimental techniques will be discussed in Chapter 5. With respect to modelling, the original theories of electrolyte solutions go back to Svante Arrhenius [8] who first suggested that chemical equilibria between ions and undissociated molecular species exists in electrolyte solutions [7]. Studies of these mixtures have provided an interesting field of research for scientists, since electrolyte solutions exhibit appreciable deviations from ideality even at room temperature and atmospheric pressure. In 1923 Debye and Hückel [40] proposed a theory to predict the activity coefficients of ions in very dilute solutions. This theory is based on the consideration of electrostatic interactions between ions in a continuum dielectric medium. The Debye-Hückel theory and other models will be discussed in Chapter 3.

1.3 Objectives of the Research

Most theories or models for the correlation of thermodynamic properties of aqueous electrolyte solutions, such as mean ionic activity coefficients and osmotic coefficients, are limited to low concentrations of the electrolytes. The majority are for single electrolytes in water at concentrations below six molal. Most existing thermodynamic models are unable to correlate solution properties at all concentrations up to saturation. On the other hand, experimental data for multicomponent aqueous solutions are confined to ternary systems with a common ion. The few measurements which have been reported for solutions without a common ion are for osmotic coefficient calculated from measurements of the activity of water. Therefore the objectives of this research in both theoretical and experimental fields are as follows:

I -To develop a model to correlate mean ionic activity coefficients in binary electrolyte solutions over a wide range of concentration and temperature and to compare the proposed model with results obtained with existing models.

- II -To attempt the prediction of mean activity coefficients in multi-component electrolyte solutions from binary data alone.
- III -To design and develop an experimental technique to measure the mean activity coefficients of electrolytes in ternary electrolyte mixtures with or without common ion.
- IV -To measure the mean activity coefficients of the salts in the following three representative systems
 - 1. NaCl-NaNO₃- H_2O (a system for reproducibility of the literature data)
 - 2. $NaBr-NaNO_3-H_2O$ (a system with a common ion)
 - 3. NaBr-Ca $(NO_3)_2$ -H₂O (a system with no-common ion)

1.4 Presentation of the Thesis

The thermodynamics of electrolyte solutions is introduced in Chapter 2. In Chapter 3, the Debye-Hückel theory and other selected thermodynamic models are reviewed. In Chapter 4, a Non-Random Factor (NRF) model for the excess Gibbs energy of electrolyte solutions is presented. The equations for mean activity coefficients of electrolytes and ions in the binary solutions are discussed. The model is tested and compared against those of Pitzer, Bromley, Meissner and Chen. In Chapter 5, Ion Selective Electrode (ISE) techniques to measure the mean ionic activity coefficients of electrolytes in multicomponent electrolyte systems are reviewed in detail. Chapter 6 contains a description of experimental apparata and the procedures to measure mean ionic activity coefficients of electrolytes in ternary aqueous systems. Chapter 7 presents experimental results and reduced data for the following three ternary systems: NaCl-NaNO₃-H₂O, NaBr-NaNO₃-H₂O, and NaBr-Ca(NO₃)₂-H₂O. In Chapter 8, a new mixing rule to predict mean activity coefficients of electrolytes in multicomponent electrolyte coefficients of electrolytes in multicomponent electrolyte coefficients of electrolytes in multicomponent electrolytes in ternary aqueous systems. Chapter 7 presents experimental results and reduced data for the following three ternary systems: NaCl-NaNO₃-H₂O, NaBr-NaNO₃-H₂O, and NaBr-Ca(NO₃)₂-H₂O. In Chapter 8, a new mixing rule to predict mean activity coefficients of electrolytes in multicomponent electrolyte mixtures is presented. Finally, in Chapter 9, original contributions and suggestions for further work are summarized.

Chapter 2

Thermodynamics of Electrolyte Solutions

2.1 Introduction

The physico-chemical state of an electrolyte in a solvent depends on the dielectric constant of the solvent. Generally, the dissociation of an electrolyte, CA, in a solvent may be stated as follows:

$$C_{\nu_{+}}A_{\nu_{-}} \rightleftharpoons \nu_{+}C^{z^{+}} + \nu_{-}A^{z^{-}}$$

$$\tag{2.1}$$

where ν_{+} and ν_{-} are stoichiometric numbers of cation $C^{z^{+}}$ and anion $A^{z^{-}}$, recipectively, and z^{+} and z^{-} are the corresponding charge numbers. In a mixture of a solvent of molecular weight M and a binary electrolyte at molality m, the mole fraction of the salt, S, and ions can be expressed as follows,

$$x_{\rm S} = \frac{m}{\nu m + 1000/M} \tag{2.2}$$

$$x_C = \frac{\nu_+ m}{\nu m + 1000/M} \tag{2.3}$$

$$x_A = \frac{\nu_- m}{\nu_m + 1000/M} \tag{2.4}$$

where the stoichiometric number of the salt is,

$$\nu = \nu_+ + \nu_- \tag{2.5}$$

Equations (2.3) and (2.4) assume total dissociation of the salt and the following relation can be written between mole fraction of salt, x_s , and mole fraction of the solvent (water).

$$\nu x_{\rm S} + x_W = 1$$

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In this chapter, the chemical potential of electrolytes in terms of mean ionic activity coefficients and mean activity coefficient of a salt in different scales will be reviewed. Finally, the Gibbs-Duhem equation for binary aqueous solutions and expressions for the osmotic coefficient will be summarized.

2.2 The Chemical Potential and the Activity of Electrolytes

For an open phase in which matter is able to enter or leave, and where surface and force fields effects are negligible, differential Gibbs energy can be written as

$$dG = -S \ dT + V dP + \sum_{j} \mu_{j} dn_{j}$$
(2.6)

where S and V are the entropy and volume of the system and n_j denotes the number of moles of species j present in the phase. At constant temperature and pressure, the chemical potential of species i is given by,

$$\mu_{i} = \left(\frac{\partial G}{\partial n_{i}}\right)_{T,P,n_{j\neq i}}$$
(2.7)

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The right hand side of equation (2.7) shows that the chemical potential is the partial molar property of the Gibbs energy with respect to species *i*. The partial molar Gibbs energy can not be measured directly. Thus, the definition of the activity a_i of species *i* in a solution provides a convenient way to express its chemical potential:

$$\mu_{i} = \mu_{i}^{\theta} + RT \ln(\frac{a_{i}}{a_{i}^{\theta}})$$
(2.8)

Following the nomenclature of Stokes [125], the superscript θ denotes an arbitrarily chosen s*andard state for the component i at the temperature of the system T and μ_i^{θ} is the standard chemical potential of i at T. It is conventional to choose the standard state so that the corresponding standard activity a_i^{θ} is unity to obtain a simpler relation:

$$\mu_{i} = \mu_{i}^{\theta} + RT \ln a_{i} \tag{2.9}$$

The activity a, of species i can also be expressed in terms of its fugacity.

$$a_i = \frac{f_i}{f_i^{\theta}} \tag{2.10}$$

where f_i^{θ} is the standard fugacity for the component *i* at the given temperature.

In aqueous electrolyte solutions, the electrolyte usually dissociates into ionic species, and it thus is convenient to develop thermodynamic equations for the ionic species. However, a standard state which recognizes the ionic character of the solution is required. This raises a problem which can not be solved experimentally because according to eq. (2.7), the physical operation, in which one can add to the solutions ions *i* only, can not be carried out. Thus, only an electrolyte solution with a balanced amount of negative charges and positive charges can be treated Nevertheless, in principle, the chemical potential of an electrolyte theoretically can be expressed as a

function of its constituents.

For aqueous solutions the activity of a salt can be expressed in terms of different concentration scales such as molality (m), molarity (c), and mole fractions (x). The most commonly used concentration scale in aqueous electrolyte thermodynamics is the molality, *i.e.*, moles per 1000g of solvent. The molality of a stable mixture does not change with temperature and pressure variations unless a phase change occurs. For ions the arbitrarily chosen standard state for the activity of species *i* is the hypothetical ideal solution of unit molality of the ion *i*. The ideal solution is chosen such that the ratio $\frac{a_1}{m_1}$ tends to unity as the molality approaches zero. This ratio can be defined as the molal activity coefficient γ_1 :

$$\gamma_{i} = \frac{a_{i}}{m_{i}} \quad (a_{i} = \gamma_{i} m_{i}) \quad ; \gamma_{i} \to 1 \quad when \quad m_{i} \to 0$$

$$(2.11)$$

and using eq. (2.11), eq. (2.9) takes the form

$$\mu_{i} = \mu_{i}^{\theta} + RT \ln\left(\gamma_{i} m_{i}\right) \tag{2.12}$$

combining eqs (2.10) and (2.11), fugacity of species *i* becomes

$$f_{i} = \gamma_{i} m_{i} f_{i}^{\theta} \tag{2.13}$$

However, eq. (2.13) is not conventional because the fugacity is usually expressed using a mole fraction scale. One can also define the chemical potential in terms of the mole fraction scale,

$$\mu_{i} = \mu_{i}^{\star} + RT \ln \left(x_{i} \gamma_{i}^{(x)} \right)$$
(2.14)

where $\gamma_i^{(x)}$ denotes the rational or mole fraction activity coefficient of species *i*. The conventional fugacity of species *i* is then expressed as:

$$f_i = \gamma_i^{(x)} x_i f_i^{\star} \tag{2.15}$$

where f_i^{\star} is the fugacity standard state of species *i*. In this case, the ideal solution is chosen such that the ratio $\frac{a_i}{x_i}$ tends to unity as the mole function approaches zero. Thus, $\gamma_i^{(x)} \to 1$ when $x_i \to 0$. The standard state fugacity corresponds to unit mole fraction of the ideal solution.

2.3 Mean Ionic Activity Coefficient

As discussed above, the thermodynamic properties for individual ionic species can not be obtained separately and must be measured for the electrolyte as whole. Considering the chemical reaction, *i.e.*, eq. (2.1), the following electroneutrality relation is valid for a binary electrolyte solution.

$$\nu_+ Z^+ + \nu_- Z^- = 0 \tag{2.16}$$

The chemical potential of salt S can be written as:

$$\mu_{\rm S} = \nu_+ \mu_+ + \nu_- \mu_- \tag{2.17}$$

where μ_+ and μ_- are the chemical potential of the cation and the anion, respectively. Using eq. (2.9) for both anion and cation:

$$\mu_{+} = \mu_{+}^{\theta} + RT \ln a_{+} \tag{2.18}$$

$$\mu_{-} = \mu_{-}^{\theta} + RT \ln a_{-} \tag{2.19}$$

Replacing eqs (2.18) and (2.19) in eq. (2.17):

$$\mu_{\rm S} = \mu_{\rm S}^{\theta} + RT \ln(a_+^{\nu_+} a_-^{\nu_-}) \tag{2.20}$$

where

$$\mu_{\rm S}^{\theta} = \nu_{+}\mu_{+}^{\theta} + \nu_{-}\mu_{-}^{\theta} \tag{2.21}$$

According to Lewis and Randall [85], the equilibrium constant of reaction (2.1) using eq. (2.11), can be written as

$$K = \frac{a_{+}^{\nu_{+}} a_{-}^{\nu_{-}}}{a_{\rm S}} = \frac{(m_{+}^{\nu_{+}} \gamma_{+}^{\nu_{+}})(m_{-}^{\nu_{-}} \gamma_{-}^{\nu_{-}})}{a_{\rm S}}$$
(2.22)

If the standard states for the ions are chosen such that there would be no difference in the standard free energies of dissociated and undissociated forms, then K is unity and the activity of the salt S can be found as [85]:

$$a_{\rm S} = a_+^{\nu_+} a_-^{\nu_-} = (m_+^{\nu_+} m_-^{\nu_-})(\gamma_+^{\nu_+} \gamma_-^{\nu_-})$$
(2.23)

where $m_{+} = \nu_{+}m$ and $m_{-} = \nu_{-}m$. The mean ionic activity coefficient is then defined as

$$\gamma_{\pm} = (\gamma_{+}^{\nu_{+}} \gamma_{-}^{\nu_{-}})^{1/\nu} \tag{2.24}$$

and eq. (2.23) takes the following form.

$$a_{\rm S} = (\nu_+^{\nu_+} \nu_-^{\nu_-}) m^{\nu} \gamma_{\pm}^{\nu} \tag{2.25}$$

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Thus, the mean activity of salt S can be written as

$$a_{\pm} = (\nu_{\pm}^{\nu_{\pm}} \nu_{-}^{\nu_{-}})^{1/\nu} m \gamma_{\pm}$$
(2.26)

Replacing eq. (2.25) in eq. (2.20), the chemical potential of the salt, S, in terms of the mean ionic activity coefficient can be expressed as

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$$\mu_{\rm S} = \mu^{\theta} + RT \ln(\nu_{+}^{\nu_{+}} \nu_{-}^{\nu_{-}}) + \nu RT \ln(m\gamma_{\pm})$$
(2.27)

or

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$$\mu = \mu^* + \nu RT \ln(m\gamma_{\pm}) \tag{2.28}$$

The mean activity coefficient, γ_{\pm} , is based on the molality scale. However, as mentioned in the previous section, the activity coefficient of electrolytes can also be expressed in terms of mole fraction (x), or in terms of molarity (c). According to Robinson and Stokes [116], the relations between various mean activity coefficients are summarized as follows:

$$\gamma_{\pm}^{(x)} = \gamma_{\pm}^{(m)} (1 + 0.001\nu Mm)$$
(2.29)

$$\gamma_{\pm}^{(m)} = \frac{c}{m\rho_s} \gamma_{\pm}^{(c)}$$
(2.30)

where $\gamma_{\pm}^{(x)}$ and $\gamma_{\pm}^{(c)}$ are the rational and molarity mean activity coefficient, respectively and ρ_s is the density of the pure solvent.

2.4 The Solvent Chemical Potential and the Osmotic Coefficient

In aqueous electrolyte solutions we are concerned with activity of water, a_W . The chemical potential of water in terms of activity of water can be presented as:

$$\mu_W = \mu_W^\theta + RT \ln a_W \tag{2.31}$$

where the standard state is the pure water at the same temperature and pressure of the solution. Hence for pure water, the activity is unity. The activity or the activity coefficient of water are not very sensitive quantities in dilute aqueous solutions. In order to exaggerate the deviations from ideality of the water, it is convenient to express the activity of water using the osmotic coefficient. For a multicomponent electrolyte solution with a solvent of molecular weight M, the osmotic coefficient is defined as follows

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$$\phi = (\frac{-1000}{M}) \frac{\ln a_W}{\sum_j \nu_j m_j}$$
(2.32)

where ν_j is the stoichiometric number of the salt j. In a sense the osmotic coefficient is analogous to the compressibility factor. As the real solution behavior tends towards ideal, the osmotic coefficient tends to unity. Following Pitzer [104], the osmotic coefficient of a mixed electrolyte solution can be written as

$$\phi = 1 - \frac{\partial G^{ex} / \partial N_W}{RT \sum_j m_j} \tag{2.33}$$

where N_W is the number of kilograms of water. Equation (2.33) can also be expressed in terms of the activity coefficient of water in a binary electrolyte solution.

$$\phi = 1 - \frac{n_W}{\nu n_S} \ln \gamma_W \tag{2.34}$$

where $n_{\rm S}$ is the number of moles of salt and n_W is the number of moles of water.

2.5 The Gibbs-Duhem Equation for Binary Aqueous Electrolyte Solutions

For a binary aqueous solution, the Gibbs-Duhem equation at constant temperature and neglecting the effect of the pressure can be written as

$$n_{\rm S}d\mu_{\rm S} + n_W d\mu_W = 0 \tag{2.35}$$

The chemical potential of both salt and water can be expressed by means of rational (mole fraction) activity coefficients so that eq. (2.35) is written as:

$$\nu x_{\rm S} d \ln \gamma_{\pm}^{(x)} + x_{W} d \ln \gamma_{W}^{(x)} = 0 \tag{2.36}$$

Alternatively, using molal mean activity coefficients, the following forms of Gibbs-Duhem equation are obtained.

$$\nu m d \ln (m \gamma_{\pm}) + (\frac{1000}{M}) d \ln a_{W} = 0$$
(2.37)

or

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$$\nu m d \ln \gamma_{\pm} + \frac{1000}{M} d \ln \gamma_{W} + \nu dm = 0$$
(2.38)

Using eqn.(2.32), eqn.(2.37) can be written as:

$$\nu m d \ln (m \gamma_{\pm}) = -(\frac{1000}{M}) d \ln a_W = \nu d(m \phi)$$
 (2.39)

By manipulation of eq. (2.39), the osmotic coefficient can be expressed in terms of the mean ionic activity coefficient:

$$\phi = 1 + \frac{1}{m} \int_0^m m d \ln \gamma_{\pm}$$
 (2.40)

conversely, given the osmotic coefficient the mean activity coefficient can be obtained by integration of eq. (2.39).

$$-\ln \gamma_{\pm} = (1 - \phi) - \int_{0}^{m} \frac{(\phi - 1)}{m} dm$$
(2.41)

Equations (2.40) and (2.41) are useful in experimental determination of mean ionic activity coefficients using isopiestic techniques (Chapter 5).

2.6 Synopsis

In this chapter the basic equations and definitions of the thermodynamics of electrolytes solutions, particularly aqueous solutions, were reviewed. The chemical potential and standard states using different concentration scales were discussed. Expressions for the chemical potential of electrolytes in binary solutions in terms of mean ionic activity coefficients and the Gibbs-Duhem equation for binary aqueous electrolyte solutions were presented. Finally, the definition of the practical osmotic coefficient was introduced and, using Gibbs-Duhem equation, the relations between mean ionic activity coefficient and osmotic coefficient were shown.
Chapter 3

Some Models for the Mean Ionic Activity Coefficient of Electrolytes in Aqueous Solutions

3.1 Introduction

The concept of activity coefficient needs a clear definition and is meaningful only when a reference solution has been chosen. It is useful to distinguish between molecular activity coefficients and ionic activity coefficients. The ionic activity coefficient can be defined for different compositions scales as mertioned in Chapter 2, *i.e.*, molality (m), mole fraction (x) or molarity (c) [73,116,136]. When ionic or molecular activity coefficients are used it is important to state the composition scale in use. Relationships between the various activity coefficients are given in Chapter 2. The difference in numerical values among different scale mean ionic activity coefficients appears for solutions with molarities higher than about 0.1 mole/l. At infinite dilution:

$$\ln \gamma_{\pm}^{(m)} = \ln \gamma_{\pm}^{(x)} = \ln \gamma_{\pm}^{(C)} = 0 \quad when \quad x_{i}^{\infty} = m_{i}^{\infty} = C_{i}^{\infty} \to 0$$

From here on we will use γ_{\pm} for the molality mean ionic activity coefficient and $\gamma_{\pm}^{(x)}$ for mole fraction or rational mean ionic activity coefficient.

The mean ionic activity coefficient is not a measurable quantity but it can be directly calculated from electromotive force measurements, particularly at low concentration. For high concentrations, the mean activity coefficient has traditionally been obtained by isopiestic methods [100,116], or from freezing point data using the following equation [73]:

$$\ln(m_{\pm}\gamma_{\pm}) = \frac{\Delta H_f^o}{R} (\frac{1}{T_o} - \frac{1}{T}) + \frac{\Delta C_P}{R} \ln(\frac{T}{T_o}) + \frac{\Delta C_P}{R} (\frac{T_o}{T} - 1)$$
(3.1)

where $\Delta T = T_o - T$ is the freezing-point depression; ΔH_f^o is the heat of fusion and ΔC_P is the heat capacity difference between the liquid and the solid phases. Some experimental techniques for the measurement of the mean ionic activity coefficients will be discussed further in Chapter 5.

After the Arrhenius [7,8,9] theory of electrolytic dissociation of electrolytes, Debye and Hückel [40] proposed a theory of ionic interactions which has been recognized as the limiting law for the mean ionic activity coefficient of strong electrolytes at very dilute solutions. The limiting law is expressed as

$$\ln \gamma_{\pm} = -AZ^+ Z^- \sqrt{I} \tag{3.2}$$

where A is the Debye-Hückel constant and I is the ionic strength of the solution introduced by Lewis and Randall [85]. The ionic strength is evaluated as follows

$$I = \frac{1}{2} \sum m_i Z_i^2$$
 (3.3)

where m_i and Z_i are molality and charge number of ion i, respectively.

In this chapter, the effects of long and short range forces are discussed. In particular, the Debye-Hückel theory and its basic aspects are examined. Finally, for binary aqueous electrolyte solutions, some previous models and their shortcomings are analyzed.

3.2 Long and Short Range Forces

In the development of thermodynamic models for electrolyte solutions one should consider at least two effects, one related to long range forces between ionic species and the other to short range forces between molecule-molecule and molecule-ion species [65,71,73]. The long range forces are electrostatic in nature and are inversely proportional to the square of the separation distance between particles. These forces have a much greater range of interaction than other forces and thus, they are referred to as long-range forces. Short range intermolecular forces such as Lenard-Jones interaction forces usually depend on the reciprocal distance to a power seven or higher. The repulsive forces only act at very short distances and thus they are considered as short-range forces. Chemical and hydrogen bonds may be treated as short range forces in some cases [81]. The ion-molecule interactions are dominated by the electrostatic forces between permanent dipoles and ions which also can be treated as short range forces in nature [81]. Other forces such as induction forces, dispersion forces and chemical forces are generally also referred to as short range forces [71].

The thermodynamic and physical properties of aqueous electrolyte solutions depend on both types of forces. The relative importance of each type depends on the concentration of salt. In concentrated solutions short range forces dominate while in the dilute solutions long-range forces control the thermodynamic behavior of the solution.

Perhaps the most important aspects of aqueous electrolyte solutions are the structure of water and the interaction of ions with water molecules. In fact, "the nature of the water-water interactions, the life time of distinguishable species of water molecules, and the fraction of hydrogen-bonded structures in the liquid water still await clarification " [46]. Many postulates have been proposed to explain the nature of intermolecular forces in aqueous solutions; however further discussion of this subject is out of the scope of the present research. Additional details may be found in several references [46,71,81,109].

3.3 The Debye-Hückel Theory

A theoretical model for completely dissociated electrolytes in water was developed by Debye and Hückel in 1923 [40]. This model is considered to be one of the cornerstones of our knowledge of the thermodynamic properties of electrolyte solutions. It has been thoroughly analyzed and discussed by many researchers with different levels of sophistication. A detailed account of the theory can be found in the literature [84,85,116,136]. This model is strictly applicable to very low concentrations up to molalities of the order of 0.01 of electrolyte in water. The Debye-Hückel theory is also referred to as the ion-cloud model, because the ions are considered to be distributed in a continuous dielectric media The basic assumptions introduced in the development of the theory are as follows,

- 1. The electrolyte solution is treated as if only anions and cations exist in the solution.
- 2. A primitive model is applied, in which the ions are regarded as charged hard spheres and the solvent is replaced by a dielectric continuum with dielectric constant, D, through the whole medium. According to the primitive model, the direct potential ψ_{ij} between ions i and j of charges Z_ie and Z_je , separated by a distance r_{ij} , is given by

$$\psi_{ij} = \frac{Z_i Z_j e^2}{D r_{ij}} \quad (r_{ij} \ge a)$$

$$\psi_{ij} = \infty \quad (r_{ij} < a)$$
(3.4)

- 3. Only long range electrostatic interactions are considered in the development of the theory. The short range interactions between water molecules and ionic species are ignored.
- 4. An ion is arbitrary chosen to be the central ionic species, surrounded by an ion cloud. The variation of the excess charge density with distance r from this central or reference ion is then considered. The charge of the cloud of ions contributes a total charge equal to that of the central ion but of opposite

sign. Thus the solution is considered as a collection of central ions with their respective ion clouds.

5. The distribution function for the cloud ions around the central ion is assumed to be of the Boltzmann distribution form:

$$g_{ij}(r) = exp(-\frac{Z_i e\psi_{ij}(r)}{kT})$$
(3.5)

Where Z, is the charge number of ion i in ion cloud and k is the Boltzmann constant. The dependence of the total electric potential on the charge distribution is expressed by Poisson's equation of electrostatics which relates the time-averaged charge density $\rho_j(r)$ and electrostatic potential $\psi_{ij}(r)$ for any distance r from the central ion of type j. Thus, the electrostatic potential, $\psi_{ij}(r)$, can be derived by using of Poisson's law and considering only the first two terms of the Taylor's expansion of the exponential term of Boltzmann distribution.

Finally, the molar electrical Gibbs-energy can be obtained as [116],

$$g_j^{ex} = -\frac{N^{\circ} Z_j^2 e^2}{2D} \frac{\kappa}{1+\kappa a}$$
(3.6)

where

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$$\kappa^{2} = \frac{4\pi e^{2} \sum n_{i} Z_{i}^{2}}{D \, k \, T} \tag{3.7}$$

The constant a is the radius of the hard sphere core. The quantity κ is sometimes described as the reciprocal thickness of the ionic atmosphere and it can be approximated by

$$\kappa = 50.2916 \times 10^8 \frac{\rho_s^{1/2}}{(TD)^{1/2}} \sqrt{I}$$
(3.8)

where I is the ionic strength as defined by eq. (3.3) and ρ_s is the density of the solvent. The activity coefficient of ion j can be obtained by using eq (3.6) and the definition of the chemical potential. Then,

$$\ln \gamma_j = \frac{-AZ_j^2 \sqrt{I}}{1 + \beta a \sqrt{I}} \tag{3.9}$$

where

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$$A = \left(\frac{e}{\sqrt{D k T}}\right)^3 \sqrt{\frac{2\pi \rho_s N^o}{1000}} = \frac{4.2013 \times 10^6 \rho_s^{1/2}}{(TD)^{3/2}}$$
(3.10)

and

$$\beta = \frac{e}{(kTD)^{1/2}} \left(\frac{8\pi N^{\circ} \rho_{s}}{1000}\right)^{1/2} = \frac{50.029 \times 10^{8} \rho_{s}^{1/2}}{(TD)^{1/2}}$$
(3.11)

The values of A and β at T=298.15K and D=78.3 (dielectric constant of water) are

$$A = 0.5108 \ln 10 = 1.1762 \ kg^{1/2} mole^{-1/2}$$

$$\beta = 0.3287 \times 10^8 \ kg^{1/2} mole^{-1/2} cm^{-1}$$

The size of the ion, a, has been reported by several investigators [73] and for most ions is close to a value of 4 angstroms. For cations such as H⁺ and Na⁺ values of 6 and 5 angstroms, respectively, have been reported. However, in most treatments the product of βa is considered as an adjustable parameter, B, with a value using between 1 to 2 kg^{1/2}mole^{-1/2}.

Finally, using the definition of the mean ionic activity coefficient,

$$\nu \ln \gamma_{\pm} = \nu_{+} \ln \gamma_{+} + \nu_{-} \ln \gamma_{-} \quad (2.24)$$

and eq. (3.9), the mean ionic activity coefficient can be obtained as

$$(\ln \gamma_{\pm})_{DH} = \frac{-A|Z^+Z^-|\sqrt{I}|}{1+B\sqrt{I}}$$
(3.12)

Alternatively, as shown by Robinson and Stokes [116], following the charging process approach of Fowler and Guggenheim [45], the molar excess Gibbs energy of an individual single ion of species j can be obtained as,

$$g_{j}^{ex} = -\frac{N^{\circ}e^{2}Z_{j}^{2}}{2D}\frac{\kappa}{1+\kappa a} + \frac{\bar{\upsilon}_{j}kT}{24\pi N^{\circ}a^{3}}(\kappa a)^{3}\sigma(\kappa a)$$
(3.13)

with

E Contraction

$$\sigma(\kappa \boldsymbol{a}) = \frac{3}{(\kappa \boldsymbol{a})^3} [1 + \kappa \boldsymbol{a} - \frac{1}{1 + \kappa \boldsymbol{a}} - 2\ln(1 + \kappa \boldsymbol{a})]$$
(3.14)

The activity coefficient of ionic species j derived from eq. (3.13) has the following form.

$$(\ln \gamma_i)_{DH} = -\frac{Z_j^2 e^2}{2D \, k \, T} \frac{\kappa}{1 + \kappa a} + \frac{\bar{v}_j}{24\pi N^o a^{-3}} (\kappa a)^3 \sigma(\kappa a) \tag{3.15}$$

As discussed by Robinson and Stokes [116], the second term of the right-hand side of eq. (3.15) is negligible at all concentrations of the electrolyte other than the extremely dilute solution so that eq. (3.15) is simplified to eq. (3.9). In addition, when the ions are assumed to be point charges, i.e., $E_{-}=0$, eq. (3.9) is simplified to eq.(3.1) which is the limiting ionic activity coefficient at extremely dilute solutions.

Pitzer used mole fraction as the measure of composition. The form obtained by Pitzer [101] was derived using pressure equation of statistical mechanics. The final equation for the electrostatic excess Gibbs energy is

$$\frac{G^{ex,el}}{RT} = -(\sum n_k) (\frac{1000}{M})^{1/2} (\frac{4A_{\phi}I_x}{\rho_s}) \ln(1+\rho I_x^{1/2})$$
(3.16)

where the sum includes all species, neutral as well as ions. Here, n_k is the number of moles of species k, M is the molecular weight of the solvent and I_x is the ionic strength of the solution on a mole fraction basis,

$$I_x = \frac{1}{2} \sum Z_i^2 x_i$$
 (3.17)

$$A_{\phi} = \frac{1}{3} \left(\frac{2\pi N^{o} \rho_{W}}{1000}\right)^{1/2} \left(\frac{e^{2}}{DkT}\right)^{3/2}$$
(3.18)

The parameter ρ is related to the closest approach of ions, *i.e.*, the sum of their effective radii in solution, but increased by the factor $(\frac{1000}{M})^{1/2}$ from the parameter B used on the molality basis. The derivative of G^{ex} yields the activity coefficient of any species.

$$\ln \gamma_{i} = -\left(\frac{1000}{M}\right)^{1/2} A_{\phi} \left[\frac{2Z_{i}^{2}}{\rho} \ln(1+\rho I_{x}^{1/2}) + \frac{Z_{i}^{2} I_{x}^{1/2} - 2I_{x}^{3/2}}{1+\rho I_{x}^{1/2}}\right]$$
(3.19)

In the case of uni-univalent salts, using eq. (3.19), the mean ionic activity coefficient of the salt can be obtained as

$$\ln \gamma_{\pm} = -\left(\frac{500}{M}\right)^{1/2} A_{\phi} \left\{\frac{2^{3/2}}{\rho} \ln\left(1 + \frac{\rho}{2^{1/2}} x_2^{1/2}\right) + \frac{x_2^{1/2} - x_2^{3/2}}{1 + \frac{\rho}{2^{1/2}} x_2^{1/2}}\right\}$$
(3.20)

where x_2 is mole fraction of the salt. Pitzer [101] obtained a value of 1.2 for B which converted by the factor $(\frac{1000}{M})^{1/2}$ yields 8.94 on a mole fraction basis. However Pitzer proposed a value of 14.9 for closest approach which is approximately constant for a wide variety of salts.

Several investigators have criticized the Debye-Hückel theory [85,112,113,116]. The major problem in the theory is the use of Boltzmann law for the radial distribution function, *i.e.*, the distribution of ions around a central ion, and "the Boltzmann law can only be applied rigorously to non-interaction particles or to particles that interact solely through elastic collision which do not affect the free energy of the system." [113] The theory is limited to very low concentrations, since short range forces are neglected. At higher concentrations attractive short range forces and even repulsive shorter range forces become important. Another shortcoming of the theory arises from the assumption that the hard-core diameter is the same for all ions in the solution. Furthermore, the theory treats water as a continuous medium in which the dielectric behavior is constant for whole range of concentration. It was shown by Hasted et al. [69] that due to the changing of the dipole moment of water and the saturation of dielectric in the neighborhood of an ion, the dielectric constant of water decreases upon increasing the concentration of the electrolyte.

3.4 Debye-Hückel Expressions for the Water Activity and the Osmotic Coefficient

The Debye-Hückel expression for the activity of water in a binary aqueous solution can be obtained using the Gibbs-Duhem eq. (2.36) as follows,

$$-\frac{1000}{M}\ln(a_W)_{DH} = \nu m + \int_0^m \nu m d(\ln \gamma_{\pm})$$
(3.21)

using Debye-Hückel expression, eq. (3.12), equation (3.21) can be rearranged as,

$$(\ln a_W)_{DH} = \frac{-\nu mM}{1000} + \frac{AM}{1000} \int_0^I \frac{\sqrt{I}}{(1+B\sqrt{I})^2} dI$$
(3.22)

Integrating eq. (3.22),

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$$(\ln a_W)_{DH} = \frac{-\nu mM}{1000} + \frac{2A_M}{(10B)^3} [1 + B\sqrt{I} - 2\ln(1 + B\sqrt{I}) - \frac{1}{1 + B\sqrt{I}}]$$
(3.23)

Equation (3.23) gives the Debye-Hückel activity of water. The activity coefficient of water $(a_W = \gamma_W x_W)$ can be readily obtained as

$$\ln(\gamma_W)_{DH} = \frac{2A_M}{(10B)^3} \left[1 + B\sqrt{I} - 2\ln(1 + B\sqrt{I}) - \frac{1}{1 + B\sqrt{I}}\right] + \ln(1 + \frac{\nu mM}{1000}) - \frac{\nu mM}{1000}$$
(3.24)

By expanding the second term and neglecting the higher order terms of the expanded equation, at high dilution eq. (3.24) takes the following form.

$$\ln(\gamma_W)_{DH} = \frac{2AM}{(10B)^3} [1 + B\sqrt{I} - 2\ln(1 + B\sqrt{I}) - \frac{1}{1 + B\sqrt{I}}]$$
(3.25)

The osmotic coefficient of water can be obtained by one of eqs (2.32), (2.33) and (2.34). For simplicity, eq. (3.25) is substituted in eq. (2.34) and the following equation is obtained.

$$\phi_{DH} = 1 - \frac{Z^+ Z^- A}{B^3 I} \left[1 + B\sqrt{I} - 2\ln(1 + B\sqrt{I}) - \frac{1}{1 + B\sqrt{I}} \right]$$
(3.26)

3.5 Models for Aqueous Electrolyte Solutions

Since the introduction of the Debye-Hückel theory for dilute solutions, there have been many attempts to reproduce the behavior of mixtures of higher molalities; Maurer [89] and Renon [114] have reviewed developments up to 1986. Generally, it is possible to group existing models into three categories:

- 1. Models based on direct extensions of the Debye-Hückel equation.
- 2. Models based on statistical molecular thermodynamics.
- 3. Models based on the local composition concept.

Although not comprehensive, this simple classification allows a systematic pattern in the study of models. However, the possibility that in the near future local compositions may be evaluated from pair correlation functions and used to extend the Debye-Hückel theory can not be ignored. It should be noted that all models included in these three classes reduce to the Debye-Hückel expression us the solution approaches infinite dilution.

3.5.1 Direct Extensions of the Debye–Hückel expression

The Debye Hückel theory takes into account only long range electrostatic forces which dominate only in very dilute solutions. Semi-empirical models developed for the mean activity coefficient by many investigators normally retain the Debye Hückel expression as the leading term. Among these models we may include the specific ionic interaction model of Guggenheim [58], the one-parameter model of Bromley [20], the graphical correlation of Meissner [92,93], and the hydration model of Stokes and Robinson [126,127].

Following the specific ion interaction approach of Bronsted [21], *i.e.*, considering that only ions of opposite sign interact, Guggenheim proposed a simple equation for the mean ionic activity coefficient of an electrolyte which consists of cation "c" and anion "a" as,

$$\ln \gamma_{\pm ca} = (\ln \gamma_{\pm ca})_{DH} + \frac{2\nu_{+}}{\nu_{+} + \nu_{-}} \sum_{a'} B_{ca'} m_{a'} + \frac{2\nu_{-}}{\nu_{+} + \nu_{-}} \sum_{c'} B_{c'a} m_{c'}$$
(3.27)

where $B_{ca'}$ and $B_{c'a}$ are called the specific ion interaction coefficients which express the contribution of the short range interactions. Some simple relations [38,39] for these coefficients have been proposed for binary aqueous electrolyte solutions and they are applicable up to molality 0.1. However, these coefficients are usually treated as adjustable parameters.

Bromley [20] proposed an empirical model which is simple and applicable to single strong electrolyte solutions up to an ionic strength of six. The model has one adjustable parameter which is correlated to two cationic and anionic parameters with a cation-anion combination. He proposed an equation of the following form.

$$\log \gamma_{\pm} = (\log \gamma_{\pm})_{DH} + B_{12}I \tag{3.28}$$

where

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$$B_{12} = \frac{(0.06 + 0.6B)|Z^+Z^-|}{(1 + \frac{1.5}{|Z^+Z^-|}I)^2} + B$$
(3.29)

and \boldsymbol{B} is the only adjustable parameter .

Meissner and Kusik [92,93] proposed a method in which they defined a quantity, $\boldsymbol{\Gamma}$, the reduced activity coefficient as,

$$\Gamma = \gamma_{\pm}^{1/|Z^+Z^-|} \tag{3.30}$$

Plotting Γ versus the ionic strength allows one to construct a family of curves in which, by having one value of γ_{\pm} above the Debye-Hückel concentration range, the mean ionic activity coefficient for any concentration could be predicted. This model is applicable for temperatures higher than 25 C° and can fit the mean ionic activity coefficient data up to an ionic strength of six.

Experimental evidence reveals that the interaction of water molecules with ionic species depends on the size and charge of the ions. Based on ionic hydration considerations, Stokes and Robinson [127] proposed a model which describes the behavior of many strong electrolyte solutions in the range of low to medium concentrations. A limitation of this model was the use of fixed hydration number, *i.e.*, the number of water molecules associated with a given ion at all concentration of salt. After, Stokes and Robinson [126] modified their model by allowing ions to be partially hydrolyzed through successive thermodynamic constants for n, n+1, ...etc water molecules per ion. Thus by decreasing hydration number with increasing concentration allows a fit of experimental mean activity coefficient of LiBr up to a molality of twenty.

3.5.2 Models Based on Statistical Molecular Thermodynamics

Models based on molecular thermodynamic approaches have been widely used to predic mean activity and osmotic coefficients of aqueous electrolyte solutions above Debye-Hückel limit. According to Lee et al. [84], using molecular thermodynamics there are two approaches, other than experiments, for obtaining the structure of fluids: 1) computer simulation using Monte Carlo (MC) or Molecular Dynamics (MD) methods and 2) integral equations such as the Percus-Yevick (PY) and the Hyper-Netted Chain (HNC) equations. Using these two approaches, there are two kinds of statistical mechanical models in which electrolyte solutions can be treated. First, the McMillan-Mayer [48,91] type of models which approximate the solvent as continuum dielectric media and only consider the interaction of ionic species. Thus, Debye-Hückel theory is a special case of McMillan-Mayer models. Second, Born-Oppenheimer type of models [48] in which the solvent species as well as the ionic

species appear explicitly in the solution.

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Based on the McMillan-Mayer theory, Monte-Carlo techniques were used to study the primitive model of an ionic solution by Card et al. [28]. The prediction of osmotic and mean activity coefficients of single uni-univalent electrolyte aqueous solutions were obtained in the range 0.01-2 m.

Kondo et al. [79] developed expressions using statistical mechanics for activity and osmotic pressures for electrolyte solutions. They proposed Coulombic and hardsphere terms (primitive model) for ionic interactions potentials and a square-well term was introduced to take care of the solvent interaction potentials. By taking the depth of the square-well as a adjustable parameter, the model was applicable up to ionic strength of three.

Integral equations based on correlation functions have been widely used for the prediction of thermodynamic properties of electrolyte solutions from a knowledge of pair potentials. One key development in the integral equation method has been the use of Mean Spherical Approximation (MSA). Application of integral equations such as the HNC and PY are limited by lack of an accurate analytical expression for the correlation functions. From a statistical mechanical point of view, in order to determine the molar Helmholtz free energy as a function of integrate (T, ρ) one needs to specify both the total h(r) and the direct c(r) correlation functions. These correlation functions are defined as,

$$h(r_{12}) = g(r_{12}) - 1 \tag{3.31}$$

$$h(r_{12}) = \mathbf{c} \ (r_{12}) + \rho \int dr_3 \mathbf{c}(r_{13}) h(r_{32}) \tag{3.32}$$

where $g(r_{12})$ is the radial distribution or pair correlation function. Equation (3.32) is called Ornstein-Zernike [94] equation. As it is evident from eqs (3.31) and (3.32), in order to determine the radial distribution function, one needs to have explicit expressions for both $h(r_{12})$ and $c(r_{12})$. The MSA is an approximation which assumes

the following forms for these functions.

$$h(r_{12}) = -1$$
 for $r_{12} < \sigma_{ij}$ $(\phi(r_{12}) = \infty)$ (3.33)

$$\boldsymbol{c}(r_{12}) = \frac{-\psi_{ij}(r)}{kT} \quad \text{for} \quad r_{12} > \sigma_{ij} \quad (r \to \infty)$$
(3.34)

where

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$$

Here σ_{ij} is the closest distance of approach for the pair and $\psi_{ij}(r)$ is the electrostatic interactive potential

$$\psi_{ij}(r) = \frac{e^2 Z_i Z_j}{D r}$$

Lebowitz and Percus [82], based on the integral equation theory of Percus and Yevick [97], proposed the use of MSA for lattice gases (neutral molecules) with extended hard cores. Waisman and Lebowitz [133,132] and Blum [16,17,18], using MSA, developed and solved exact analytical solutions for a primitive model (charged spheres) of electrolyte solutions.

There are other models such as the fluctuation theory which was proposed by Kirkwood and Buff [77] and further developed by Cabezas et al. [26] and by Perry et al. [98] using MSA for strong electrolyte solutions. Copeman [33] developed a perturbed hard-sphere equation of state for solutions containing an electrolyte. The equation consists of hard-sphere, electrostatic and attractive contributions to the Helmholtz free energy. Planche and Renon [99] and Ball et al. [10] also developed a semiempirical expression for the Helmholtz energy of mixed electrolyte solutions in solvent mixtures. This expression is obtained from the solution of MSA by introducing the consideration of short-range (Dirac) forces. Copeman and Stein [34] developed an explicit non-equal diameter MSA model for electrolytes. The predicted internal energy of the electrolyte solutions were compared with those of Blum for ion sizes up to 3A°. Harvey et al. [69] also developed a MSA solution based on a linear mixing rule for a single effective ion size and a low-ion-density approximation due to Copeman and Stein [34]. The results obtained for aqueous electrolyte solutions, using the primitive model, are comparable with published Monte Carlo data. Anderson and Chandler [5,6] developed the exponential MSA (EXP-MSA) which was used by Gering et al. [55] to determine the thermodynamic properties of electrolyte solutions as a function of composition and temperature for binary and mixed-salt solutions at high electrolyte concentrations. In most electrolyte theories using MSA, the diameter of ionic species or sometimes diameter of water is used as an adjustable parameter to fit osmotic or mean activity coefficients of electrolyte solutions.

Following the McMillan-Mayer solution theory, Pitzer [105], in a semiempirical way, introduced a virial expansion to complement the Debye-Hückel term in the expression of the excess Gibbs energy of electrolyte solutions

$$\frac{G^{ex}}{n_W RT} = f_{DH}(I) + \sum_{i} \sum_{j} \lambda_{ij}(I) m_i m_j + \sum_{i} \sum_{j} \sum_{k} \mu_{ijk} m_i m_j m_k$$
(3.35)

where $f_{DH}(I)$ is an electrostatic Debye-Hückel osmotic term which is obtained by substituting the Debye-Hückel radial distribution function in the pressure equation of statistical mechanics. The parameter $\lambda_{ij}(I)$ is a binary short-range interaction term which is dependent on the ionic strength and μ_{ijk} is a termary short-range interaction term which is independent of ionic strength. From eq. (3.35) the osmotic coefficient, ϕ , and mean ionic activity coefficient, γ_{\pm} , expressions have been obtained [102,103,104,106,107]. The Pitzer model has been widely used to predict ϕ and γ_{\pm} for aqueous electrolyte mixtures and is applicable up to a molahity of six

3.5.3 Models Based on the Local Composition Concept

The third class of models use empirical expressions to express the effect of local composition. As do other models for electrolyte solutions, models of this class recognize the existence of both long-range and short-range forces in electrolyte solutions. The ion-ion interactions are long-range forces that are determinant on the behavior of dilute electrolyte solutions. Short-range forces are mostly due to interactions between the ions and the solvent molecules and, as in systems of non-electrolytes, may be associated with local composition effects. The Fowler-Guggenheim version of the Debye-Hückel or the Pitzer version of the Debye-Hückel theory are applied to account for long-range contributions. For short-range contributions, various local composition treatments such as those of Wilson [75], Non-Random Two Liquid (NRTL) models, etc. have been applied. For the NRTL the hypothetical pure state of ions [31] and the random state of ions through the Non-Random Factor (NRF) as a reference state [61] have been used.

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In their most general formulation, local composition models consider that, due to the presence of short range forces, the composition in the immediate neighborhood of a given species is different from that in the bulk of the mixture. The local composition effect is usually expressed in the form

$$\frac{X_{ji}}{X_{ki}} = \frac{X_j}{X_k} \tau_{ijk}$$
(3.36)

where X_j and X_k are the bulk mole fractions of species j and k. The term X_{ji} represents the (local) mole fraction of species j around species i and , similarly, X_{ki} is the (local) mole fraction of species k around species i. The term τ_{ijk} , usually of exponential form, is related to the relative strength of potentials between species i, j and k. Local composition models have been used to develop excess Gibbs energy functions which are then differentiated to obtain mean ionic activity and osmotic coefficients.

Cruz and Renon [36] proposed to use both the Fowler and Guggenheim version of the Debye-Hückel theory and the Debye-McAulary [116] 'heories for long-range forces and NRTL local composition model for short-range forces, which were assumed to cause total hydration of ionic species. The resulting model had four adjustable parameters and was applicable over the whole concentration range for aqueous solutions of a single electrolyte. Chen et al. [30,31] proposed a new local composition model using the Pitzer version of the Debye-Hückel term for long-range forces and a modified NRTL for short-range forces. The model of Chen et al. includes two key assumptions. First, it assumes that there is no interaction between similar ionic species (like-ion repulsion). This assumption is in agreement with the theory of the specific interactions of Brönsted [18]. Second, it assumes that the distributions of cations and anions around a central solvent molecules is such that the net local ionic charge is zero (local electroneutrality). The resulting model has two adjustable parameters and reproduces well the activity coefficients of single electrolytes in water up to a molality of six. Ball et al. [10] modified the Cruz-Renon model [36] and reduced the adjustable parameters from four to two. The resulting model was used to fit osmotic coefficients of single-electrolyte solutions and compared with other two-parameter models using data up to a molality of six. Other models have extended group methods to electrolytes such as the Kawaguchi et at [75,76] version of ASOG which assumes total hydration of ions. They used the Fowler-Guggenheim-Debye-Huckel term for long-range mean ionic activity coefficients. The UNIFAC-type model of Christensen et al. [32], uses a Debye-Hückel term for electrostatic interactions and both a Brönsted-Guggenheim term [59] and an UNIQUAC [1] term for short-range forces

This study proposes a new local composition model using the Fowler-Guggenheim version of Debye-Hückel model for long-range electrostatic forces [61]. For short range contribution, a new version of NRTL using non-random factors is used. The model is successful and it appears to be the most accurate two-parameter model for aqueous solutions of single electrolytes. It can fit mean activity coefficient data for all binaries from dilute solutions up to the saturation point. Details of this model will be discussed in Chapter 4.

Liu et al. [86] derived a new version of the Debye-Hückel theory which is based on the Poisson equation of electrostatic theory, the Boltzmann distribution law and the local composition concept. For short range forces, Liu et al. [86] derived a local composition expression similar to Chen's approach except that the local composition concept applies to the excess enthalpy instead of the excess Gibbs energy. The excess Gibbs energy was obtained by integrating the Gibbs-Helmholtz equation This model has one adjustable parameter. Liu et al. [87] modified the local-composition expression for short range contribution. The new version of Liu's local composition has two adjustable parameters, one of the parameter represents the ion specific potential and the other is an energy adjusting parameter which accounts for the effects of the interaction energy strengths and the species sizes. The new version of local composition model fitted the mean activity coefficient of LiBr in water at 25 C° up to molality 20.

Ananth et al. [2] have recently proposed c self-consistent local composition model using Pitzer version of Debye-Hückel term for electrostatic long-range forces. For short range forces, the quasichemical lattice theory of Guggenheim using the self-consistent assumption of correct pair counting [96] was applied. However the model ignores size and shape factors so that the description is made in terms of local composition variables. In spite of mathematical complexity of the osmotic and mean activity coefficient expressions, the model was used to fit the osmotic coefficient of some aqueous electrolyte solution up to molality 20. The model has two adjustable parameters.

3.6 Synopsis

In this chapter the modelling of long and short range forces, which is an important aspect of electrolyte solutions, was discussed. The Debye-Hückel theory and its basic assumptions were explained. Debye-Hückel expressions for mean ionic activity and osmotic coefficients were presented. The Fowler-Guggenheim and Pitzer versions of Debye-Hückel theory for excess Gibbs energy and mean activity coefficients were introduced. Finally, previous thermodynamic models for the mean activity and osmotic coefficients were reviewed. The models were arbitrarily classified in the three following groups: 1) Models based on direct extensions of the Debye-Hückel equation, 2) models based on statistical molecular thermodynamics, and 3) models based on the local composition concept.

Chapter 4

A Non–Random Factor Model for the Excess Gibbs Energy of Electrolyte Solutions

4.1 Introduction

A typical limitation of all two-parameter local composition models previously proposed in the literature is the inability to correlate activity coefficients (or osmotic coefficients) beyond a molality of six which, incidentally, is close to the saturation molality of sodium chloride. For many industrial processes, such as crystallization of salts other than sodium chloride or work with drilling muds, it is necessary to have models able to represent the thermodynamic behavior at higher molalities. In this chapter a new formulation to represent the deviations from ideality of electrolyte solutions is discussed. The model is applicable from dilute solution up to saturation. Results from the model are compared with those obtained from other two-parameter or one parameter models of Meissner, Bromley, Pitzer and Chen et al. It should be noted that the model presented in this chapter has been already published in AIChE Journal in 1988 [61]. In this chapter we follow the content of the paper with some

4.2 A New NRTL-NRF Model

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Following the work of Chen et al. [30,31], we assume that the excess Gibbs energy of an aqueous electrolyte solution may be expressed as the sum of a contribution due to long-range coulonibic interactions and a contribution due to short-range interactions causing local order. For the long-range interactions we use the Debye-Hückel expression and for the short-range interactions we use a new version of NRTL model of Renon and Prausnitz [115] in terms of non-random factors (NRF) formally similar to those proposed by Panayiotou and Vera [96], and thus we write,

$$g^{ex} = (g^{ex})_{DH} + (g^{ex})_{NRTL-NRF}$$

$$(4.1)$$

where $(g^{ex})_{DH}$ is the Debye-Hückel contribution to the excess Gibbs energy as given for a single ion, by eq. (3.13).

The excess Gibbs energy due to the short-range effects, $(g^{ex})_{NRTL-NRF}$, arises from molecule-molecule, molecule-ion and ion-ion interactions at high concentrations. To express these effects, we follow Chen et al. [30,31] and assume the existence of three types of cells as shown in Figure (4.1). These cells, which depend on the central species are assumed to be determinant, in the microstructure of an aqueous solution of a single electrolyte. Two types of cells are those with a cation or with an anion as central species. For these cells Brönsted theory (like-ion repulsion) leads to the assumption that the local mole fraction of cation around cation and of anion around anion is zero. Thus, only solvent molecules and counterion species surround a particular ion. The third type of cell has solvent central molecules with anions, cations and solvent molecules in the surrounding. Thus, the molar excess Gibbs energy due to short-range interactions is considered to be the sum of the excess Gibbs energy of individual cells weighted by their mole fractions as follows,

$$\left(\frac{g^{ex}}{RT}\right)_{NRTL-NRF} = x_A \frac{g^{ex}_A}{RT} + x_C \frac{g^{ex}_C}{RT} + x_W \frac{g^{ex}_W}{RT}$$
(4.2)



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Figure 4.1: The various central cells in a binary electrolyte solution.

where g_A^{ex} , g_C^{ex} and g_W^{ex} represent the contributions of the cells with central anions A, central cation C and central solvent molecule W to excess Gibbs energy arising from short-range interactions. In a major departure from the NRTL model [115] and from Chen's et al. extension [30,31] to electrolytes, we consider here that the excess Gibbs energy contributions of the cells with different central species are expressed with respect to the random case instead of considering them with respect to hypothetical cells of pure central species. Thus,

$$g_A^{ex} = g_A - g_A^o \tag{4.3}$$

$$g_C^{ex} = g_C - g_C^o \tag{4.4}$$

and

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$$g_W^{ex} = g_W - g_W^o \tag{4.5}$$

by assuming the interaction energy between the different species as Gibbs energy, the Gibbs energy of the cells in terms of local mole fraction may be written as,

$$g_A = X_{WA} g_{WA} + X_{CA} g_{CA} \tag{4.6}$$

$$g_C = X_{WC} g_{WC} + X_{AC} g_{AC}$$
(4.7)

and

$$g_W = X_{WW} g_{WW} + X_{CW} g_{CW} + X_{AW} g_{AW}$$
(4.8)

for the three types of the cells. The terms g_{WA} , g_{WC} , g_{WW} are the interaction Gibbs energies between the various species. In our case, for the reference cells in the random case

$$g_A^o = X_W g_{WA} + X_C g_{CA} \tag{4.9}$$

$$g_C^o = X_W g_{WC} + X_A g_{AC} \tag{4.10}$$

and

$$g_{W}^{\circ} = X_{W} g_{WW} + X_{C} g_{CW} + X_{A} g_{AW}$$

$$\tag{4.11}$$

thus, in this new approach g_i^o considered as the Gibbs free energy of a cell when the random array prevails. In Chen's approach [30,31], g_i^o considered as the Gibbs free energy of a hypothetical cell of pure species i assumption which is not realistic for ionic species.

For generality, following Chen's et al. [30], we have used effective mole fractions defined as,

$$X_A = Z_A x_A = Z_A \nu_A x_S \tag{4.12}$$

$$X_{C} = Z_{C} x_{C} = Z_{C} \nu_{C} x_{S} \tag{4.13}$$

and

$$X_{W} = x_{W} \tag{4.14}$$

using electroneutrality, $Z_C \nu_C = Z_A \nu_A$, from eqs (4.12) and (4.13) we observe that $X_A = X_C$, which is the condition of electroneutrality of the local ionic cells.

In NRTL and related models, a parameter α , closely related to the inverse value of the coordination number z, is interpreted as a measure of non-randomness. In this work the non-randomness of the species is represented by means of non-random factor (NRF). Thus, in general, for i - j interactions

$$X_{ij} = X_i \Gamma_{ij} \tag{4.15}$$

where X_{ij} and Γ_{ij} are the local composition and the non-random factor of species *i* surrounding species *j*. Similarly,

$$X_{\ell_2} = X_{\ell} \Gamma_{\ell_2} \tag{4.16}$$

from which:

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$$\frac{X_{ij}}{X_{\ell j}} = \frac{X_i}{X_\ell} \frac{\Gamma_{ij}}{\Gamma_{\ell j}}$$
(4.17)

However, in this work the NRF are not obtained from the quasichemical theory [96] but are evaluated using the empirical Wilson [135] type expressions similar to those used by Renon and Prausnitz [115] and by Chen et al. [30,31] Thus, the NRTL equation can be written as

$$\frac{X_{ij}}{X_{\ell j}} = \frac{X_i}{X_\ell} \beta_{ij,\ell j} \tag{4.18}$$

with

$$\beta_{ij,\ell_j} = exp(-\frac{g_{ij} - g_{\ell_j}}{ZRT})$$

$$(4.19)$$

comparing eqs (4.17) and (4.18),

$$\Gamma_{ij} = \Gamma_{\ell j} \beta_{ij,\ell j} \tag{4.20}$$

and, in particular, when $\ell = j$,

$$\Gamma_{ij} = \Gamma_{jj} \beta_{ij,jj} \tag{4.21}$$

It should be clear that after choosing to use the empirical Wilson-type expression, eq. (4.18), to relate the non-random factors, our final model has the same theoretical limitations and practical advantages of all other models based on these expressions [130]. Among the practical advantages, it is interesting to observe that the final model has only two adjustable parameters for a system of a single electrolyte dissolved in a single solvent. This can be shown by eliminating variables as follows. For the energy parameters we have the following relations:

$$g_{CA} = g_{AC} = g_E \tag{4.22}$$

$$g_{AW} = g_{WA} \quad \& \quad g_{CW} = g_{WC} \tag{4.23}$$

In addition, assuming local electroneutrality around a central molecule of solvent, ic, the net charge of a central solvent cell is zero,

$$Z_A X_{AW} = Z_C X_{CW} \tag{4.24}$$

where

$$X_{AW} = X_A \Gamma_{AW} = Z_A x_A \Gamma_{AW} \tag{4.25}$$

$$X_{CW} = X_C \Gamma_{CW} = Z_C x_C \Gamma_{CW} \tag{4.26}$$

combining eqs (4.24), (4.25) and (4.26) and considering the expression for the overall electroneutrality of the solution $(Z_4x_A = Z_Cx_C)$, one obtains

$$\Gamma_{AW} = \Gamma_{CW} \tag{4.27}$$

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using eq. (4.21), Γ_{AW} and Γ_{CW} can be written as follows,

$$\Gamma_{AW} = \Gamma_{WW} \beta_{AW,WW} \& \Gamma_{CW} = \Gamma_{WW} \beta_{CW,WW}$$
(4.28)

then eqs (4.27) and (4.28) give

$$g_{AW} = g_{CW} = g_{EW} \tag{4.29}$$

thus, relations (4.22), (4.23) and (4.29) reduce to only two independent variables and from eq. (4.19) we may write

$$\beta_{CA,WA} = \beta_{AC,WC} \equiv \beta_E \tag{4.30}$$

$$\beta_{AW,WW} = \beta_{CW,WW} \equiv \beta_W \tag{4.31}$$

to simplify the notation we define the related terms arising from eq. (4.19) as

$$\lambda_E = \frac{g_E - g_{EW}}{RT} \tag{4.32}$$

and

$$\lambda_W = \frac{g_{EW} - g_{WW}}{RT} \tag{4.33}$$

the terms λ_E and λ_W are the only two adjustable parameters for an aqueous solution of a single electrolyte assumed to be completely dissociated. The parameters λ_E and λ_W are designated from here on as the electrolyte and the solvent (water) parameters, respectively.

Using eqs (4.12) and (4.13), in order to express the contribution to the excess Gibbs energy due to short-range effects in terms of the above two adjustable parameters, we observe that for the electrolyte the effective (charge) mole fractions of cation and anion are equal due to the condition of overall electroneutrality, *i.e.*,

$$X_A = X_C \equiv X_E \tag{4.34}$$

thus, starting with the cation central cell we may write an equation of the form:

$$X_{AC} + X_{CC} + X_{WC} = 1 \tag{4.35}$$

Writing the local compositions in terms of NRF's and using the Brönsted principle $(X_{CC}=0)$,

$$X_A \Gamma_{AC} + X_W \Gamma_{WC} = 1 \tag{4.36}$$

using eq. (4.20), Γ_{WC} can be written as

$$\Gamma_{WC} = \Gamma_{AC} \beta_{WC,AC} = \frac{\Gamma_{AC}}{\beta_{AC,WC}}$$
(1.37)

substituting eq. (4.37) in (4.36),

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$$\Gamma_{AC} = \frac{\beta_{AC,WC}}{X_A \beta_{AC,WC} + X_W} \tag{4.38}$$

similarly, for the anion central cell we can obtain,

$$\Gamma_{CA} = \frac{\beta_{CA,WA}}{X_C \beta_{CA,WA} + X_W} \tag{4.39}$$

then, using relations (4.30) and (4.34),

$$\Gamma_E = \Gamma_{AC} = \Gamma_{CA} = \frac{\beta_E}{X_E \beta_E + X_W} \tag{1.40}$$

and similarly for the solvent central cells,

$$X_{CW} + X_{AW} + X_{WW} = 1 (4.41)$$

where

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$$X_{CW} = X_C \Gamma_{CW} = X_C \Gamma_{WW} \beta_{CW,WW}$$
(4.42)

$$X_{AW} = X_A \Gamma_{AW} = X_A \Gamma_{WW} \beta_{AW,WW}$$
(4.43)

using relations (4.31) and (4.34) and combining eqs (4.42), (4.43) with eq. (4.41),

$$(X_A + X_C) \,\Gamma_W \,\beta_W + X_W \,\Gamma_W = 1$$

or

$$\Gamma_{W} = \frac{1}{(X_{A} + X_{C})\beta_{W} + X_{W}} = \frac{1}{2X_{E}\beta_{W} + X_{W}}$$
(4.44)

where $\Gamma_W = \Gamma_{WW}$. It should be noted that in the publication, Γ_W in eq. (19a) should read Γ_{WC} .

Having the non-random factors, *i.e.*, eqs (4.38) and (4.39), the excess Gibbs energy of the cation central cell can be obtained by substituting eqs (4.10) and (4.7) in eq. (4.4). Thus, writing the local compositions in terms of NRF's and dividing the resultant equation by "RT"

$$\frac{g_C^{ex}}{RT} = \frac{1}{RT} (X_W \, \Gamma_{WC} g_{WC} + X_A \, \Gamma_{AC} g_{AC} - X_W \, g_{WC} - X_A \, g_{AC}) \tag{4.45}$$

using eq. (4.36) for both the non-random case and also for the random case with $\Gamma_{AC} = \Gamma_{WC} = 1$, one can obtains

$$\frac{g_C^{ex}}{RT} = X_A (\Gamma_{AC} - 1) \lambda_E \tag{4.16}$$

similarly,

$$\frac{g_A^{ex}}{RT} = X_C (\Gamma_{CA} - 1) \lambda_E \tag{4.47}$$

Following the same procedure, by substituting eqs (4.8) and (4.11) in eq. (4.5) and using eq. (4.41) for the non-random case and also for the random case with $\Gamma_{AW} = \Gamma_{CW} = \Gamma_{WW} = 1$, the excess Gibbs energy of the solvent central cell can be written as,

$$\frac{g_W^{ex}}{RT} = -X_W(\Gamma_W - 1)\lambda_W \tag{4.48}$$

Finally by substituting eqs (4.46), (4.47) and (4.48) in eq. (4.2) and using eqs (4.12) and (4.13), the excess Gibbs energy of the mixture is as,

$$\left(\frac{g^{ex}}{RT}\right)_{NRTL-NRF} = \left(Z_A + Z_C\right) x_A x_C (\Gamma_E - 1) \lambda_E - x_W^2 (\Gamma_W - 1) \lambda_W \tag{4.49}$$

where λ_E and λ_W are the two adjustable parameters given by eqs (4.32) and (4.33). Clearly for the random case, $\Gamma_E = \Gamma_W = 1$, and eq. (4.49) vanishes in agreement with the local composition concept. However, it must be clearly stated that due to the simplifying assumptions of this phenomenological derivation, especially the like-ion repulsion assumption and the use of Wilson-type non-random factors, the balance equations for each cell do not extend to the overall mixture.

Following Robinson and Stokes [116], we may express eq. (4.49) in terms of a salt mole fraction as,

$$x_{\rm S} = \frac{n_{\rm S}}{n_W + \nu n_{\rm S}} \tag{4.50}$$

from which, the solvent mole fraction is obtained as:

$$x_{W} = 1 - \nu x_{\rm S} \tag{4.51}$$

Thus, using $x_A = \nu_A x_S$ and $x_C = \nu_C x_S$, eq. (4.49) takes the form:

$$\left(\frac{g^{ex}}{RT}\right)_{NRTL-NRF} = \nu_A \nu_C (Z_A + Z_C) x_{\rm S}^2 (\Gamma_E - 1) \lambda_E - x_W^2 (\Gamma_W - 1) \lambda_W \tag{4.52}$$

It should be noted that eq. (4.52) is a general equation for all single electrolyte solutions which is a little different from eq. (22b) in the publication. Equation (22b)is true for all of the binaries except bi-bivalent electrolyte solutions. The reason is that the right hand side equality of eqs (6a) and (6b) in the paper are not true for bi-bivalent electrolytes. In the derivation of eq. (4.52) we used eqs (4.12) and (4.13)which are applicable for all salts. On the other hand, the new version gives better results for bi-bivalent electrolyte solutions.

4.2.1 Expression for the Mean Ionic Activity Coefficient

As discussed by Hala et al. [60] the mean ionic activity coefficient of an electrolyte in an aqueous solution may be obtained from the relation

$$\nu \ln \gamma_{\pm} = \frac{\partial}{\partial n_{\rm S}} \left(\frac{ng^{ex}}{RT}\right)_{nw} \tag{4.53}$$

For the contribution of long-range interactions to the excess Gibbs energy (the Debye-Hückel model) the unsymmetrical normalization is used, *i.e.*, the activity coefficient of electrolyte approaches unity as its mole fraction goes to zero, but activity coefficient of solvent approaches unity as its mole fraction goes to one. Thus, it is necessary to normalize the contribution due to short-range interactions on the same basis. Therefore we use

$$\left(\frac{g^{ex}}{RT}\right)_{NRTL-NRF}^{*} = \left(\frac{g_{ex}}{RT}\right)_{NRTL-NRF} - \nu x_{\rm S} \ln \gamma_{\pm}^{\infty} \tag{4.54}$$

or in terms of the ionic activity coefficients it can be written as,

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$$\left(\frac{g^{ex}}{RT}\right)_{NRTL-NRF}^{*} = \left(\frac{g_{ex}}{RT}\right)_{NRTL-NRF} - x_C \ln \gamma_C^{\infty} - x_A \ln \gamma_A^{\infty}$$
(4.55)

where the superscript ∞ is used to indicate the value of the function at infinite dilution. The non-random factors, eqs (4.38), (4.39) and (4.44), can be written in terms of the electrolyte mole fractions as

$$\Gamma_E = \frac{\beta_E}{Z_E \nu_E x_S \beta_E + x_W} \tag{4.56}$$

$$\Gamma_W = \frac{1}{2\nu_E Z_E x_S \beta_W + x_W} \tag{4.57}$$

where

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$$Z_E \nu_E = Z_C \nu_C = Z_A \nu_A$$

Using eqs (4.56) and (4.57), from eqs (4.52) and (4.53) we obtain

$$\ln \gamma_{\pm}^{\infty} = \left(\frac{2Z_E\nu_E}{\nu}\beta_W - 1\right)\lambda_W \tag{4.58}$$

and then from eqs (4.54) and (4.58)

$$\left(\frac{g^{ex}}{RT}\right)_{NRTL-NRF}^{*} = \nu_A \nu_C (Z_A + Z_C) x_S^2 (\Gamma_E - 1) \lambda_E - x_W^2 (\Gamma_W - 1) \lambda_W + x_S (\nu - 2Z_E \nu_E \beta_W) \lambda_W$$
(4.59)

Hence, from eqs (4.53) and (4.59), the expressions for the activity coefficients of salts in the unsymmetrical convention take the form

$$(\ln \gamma_{\pm}^*)_{NRTL-NRF} = Z_E \nu_E x_S \lambda_E [(1+x_W)(\Gamma_E-1) + x_S x_W (\frac{\nu - Z_E \nu_E \beta_E}{\beta_E}) \Gamma_E^2]$$

$$+x_{W}^{2}\lambda_{W}(\Gamma_{W}-1)$$

$$-\lambda_{W}(x_{W}^{3}\Gamma_{W}^{2}-1)(1-\frac{2Z_{E}\nu_{E}}{\nu}\beta_{W}) \qquad (4.60)$$

The activity coefficient of the solvent (water) is

$$(\ln \gamma_W^*)_{NRTL-NRF} = \nu_A \nu_C (Z_A + Z_C) x_S^2 \lambda_E [1 - \Gamma_E + x_S (\frac{Z_E \nu_E \beta_E - \nu}{\beta_E}) \Gamma_E^2]$$
$$- x_W \lambda_W (2 - x_W) (\Gamma_W - 1)$$
$$- x_S x_W^2 \Gamma_W^2 \lambda_W (2Z_E \nu_E \beta_W - \nu)$$
(4.61)

Again, eqs (4.60) and (4.61) are different from eqs (29) and (30) of the publication. Finally, the mean ionic activity coefficient of a single salt in a single solvent can be written as

$$\ln \gamma_{\pm} = (\ln \gamma_{\pm})_{DH} + (\ln \gamma_{\pm}^{*})_{NRTL-NRF}$$
(4.62)

where the Debye-Hückel contribution is given by eq. (3.12). It should be noted that eq. (3.12) is based on the molality scale, while the NRTL-NRF eq. (4.60) uses mole fraction as the composition variable. However, as it was shown in Chapter 3, the Debye-Hückel expression is valid at very low concentrations in which the numerical value of the activity coefficient is the same irrespective of the concentration scales. We will further illustrate this fact at the end of the next section by showing the different contributions to the activity coefficients for the aqueous solution of HCl and KOH.

Similarly, the activity coefficient of the solvent (water) can be obtained by the sum of eqs (3.24) and (4.61).

4.2.2 Results and Discussion

The new model developed in this study is based on the Debye Hückel theory for electrostatic forces (long-range forces) and a new NRTL-NRF model for the effect of local order (short-range forces). The use of the non-random factors (NRF) and of a random liquid as a reference fluid permits the development of a model applicable to the whole range of concentration from the dilute region up to the saturation point of each salt. Figure (4.2) shows the detail of both contributions, i.e. long- and shortrange forces, to the activity coefficients of HCl in an aqueous solution. The model developed in this work has been tested for many salts. Results for the fitting of the mean ionic activity coefficients for uni-univalent electrolytes are shown in Table (4.1)As can be observed from Table (4.1), the model is able to predict the mean ionic activity coefficients of salts beyond the traditional molality of six that has been the limit set by most investigators. Some results for uni-univalent electrolytes up to molality 20 are shown in Figure (4.3). Figures (4.4) and (4.5) present a comparison of the results obtained with the most commonly used models and with new model for HCl and KOH. The two-parameter model of Ball et al [21] was not included in the comparisons since its parameters were evaluated using data of osmotic coefficients and a comparison in terms of mean ionic activity coefficient would be unfair. In fact, Ball's et al. comparison of their model with those of Chen et al. [31] and Pitzer et al. [107] was done in terms of osmotic coefficients and used parameters specifically fitted with osmotic coefficient data. The model developed in the present study yields standard deviations of less than 2.5% for HCl and less than 4% for KOll at whole range of concentration. Table (4.2) shows the results of the fit for molality mean ionic activity coefficients for non-uni-univalent electrolytes at 298-15K to maximum molality of six Figure (4.6) presents results for bi-univalent electrolytes. The model developed in the present study yields standard deviations for $CaBr_2$ and $CaCl_2$ of 7.2% and 2% while Chen's et al. model produces standard deviations of 35.1% and 20.5%, respectively As Table (4.3) shows, the results for bi-bivalent electrolyte have been improved from the publication [14] by using the new version of the model

The assumption of a completely dissociated electrolyte may be considered as limiting for the application of the present model to molecular electrolyte species and complex ions in solution. However the model was used for electrolytes such as H_2SO_4

1	Max		Std Dev		
Electrolyte	Molahty	λ_E	λ_W	of In values	
HCl	16	-9 822	16 151	0 024	
HBr	11	-10 722	19 862	0 040	
HI	10	-10 433	20 069	0 062	
HCIO4	16	-11 897	22 251	0 129	
IICIO4	10	-11 050	20 034	0 060	
HCIO4	6	-10 154	17 695	0 026	
HNO3	28	-6 971	9 007	0 018	
LiCl	20	-10 072	16 262	0 052	
LiBr	20	-11 465	20 516	$0 \ 095$	
LiBr	6	-10 651	18 525	0 045	
LiI	3	-4 505	9 584	0 020	
LIOH	5	-9 898	11 173	0 021	
LiClO₄	45	-7 662	12 996	0 017	
LiNO ₃	20	-7 616	10 450	0 016	
NaF	1	-7 382	6 967	0 002	
NaCl	6 144	-8 318	$10\ 209$	0 011	
NaBr	9	-8 357	11 000	0 061	
Nal	12	-9 246	$13 \ 370$	0.028	
NaOH	29	-10 217	14 178	0 08 1	
NaOH	20	-10502	14 952	0 057	
NaClO ₃	3	-3 975	3 390	0 005	
NaClO ₄	6	-7 002	7 461	0 009	
NaBrO ₃	2 617	-7 910	6 778	0 002	
NaNO ₃	10	-9 151	9 169	0 072	
NaH ₂ PO ₁	65	-9 434	8 458	0 003	
NaH2AsO4	13	-4 477	1 721	0 010	
NaCNS	18	-8 046	10 508	0 039	
KF	175	-9 224	11 750	0 018	
KF	6	-8 646	10 705	0 006	
KCI	5	-3 806	3 995	0 021	
KBr	55	-7 329	7 752	0 004	
KI	4 5	-0 736	3 430	0 005	
КОН	20	-10 155	15 710	0 039	
KClO ₃	0 70	-5 558	0 279	0 002	
KBrO3	04	-6 549	1 894	0 001	
KNO3	3 5	-9 097	6 945	0 004	
KH ₂ PO ₄	18	-10 794	10 867	0 002	
KH ₂ AsO ₄	13	-8 723	6 704	0 002	
KCNS	5	-6 565	6 252	0 003	
KPF ₆	05	-15 100	30 36	0 000	
RbF	3 5	-3 556	5 333	0 009	
RbCl	78	-7 941	8 144	0 003	

Table 4.1. Fit of the molality mean ionic activity coefficient data of pure aqueous uni-univalent electrolytes at 298.15K (Hamer and Wu, 1972)

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	Max	1	Ţ	Std Dev
Electrolyte	Molality	λ_E	λ_W	of In values
RbBr	5	-7 937	7 987	0.001
Rbl	5	-8 167	8 342	0.002
RbNO ₃	45	-9 375	7 260	0.007
CsF	35	5 808	7 893	0.007
CsCl	11	-8 430	8 416	0.013
CsBr	5	-8 961	9 225	0.005
CsI	3	-8 874	8 824	0.005
CsOH	12	-4 790	7 992	0.012
$CsNO_3$	15	-10 894	11 191	0 000
AgNO ₃	15	-8 527	5 523	0.014
TICIO ₄	0 5	-11928	15 157	0 001
TINO ₃	04	-16 198	40 794	0.002
TINO ₂	14	-17 167	40 858	0.003
NH₄Cl	7 405	-7 021	7 030	0.002
NH₄ClO₄	21	-10 776	$12 \ 432$	0.007
NH ₄ NO ₃	25	-7 509	5.670	0.010
Li p-tol	15	-6 231	6 100	0.014
Na p-tol	4	-4 276	2 227	0.014
K p-tol	3 5	-4 858	0.738	0 020
Na-formate	3 5	-3654	4 755	0.008
Li-acetate	1	-6 631	8 202	0.005
Na-acetate	35	-3 401	6 434	0 009
K-acetate	35	-3 273	6 844	0.008
Rb-acetate	35	-2589	6 708	0 008
Cs-acetate	35	-3 361	7 165	0.008
Tl-acetate	6	-8 357	7 144	0.010
Na-propionate	3	-3 340	7 237	800.0
Na-butyrate	35	-3 300	7 799	0.026
Na-valerate	2	-3 321	7 984	0 017
Na-caproate	23	-3.276	8.156	0.015
Na-heptylate	5	-4613	1 224	0.167
Na-heptylate	05	-3 170	8 1 1 2	0 00 1
Na-caprylate	3	-7 224	0 005	0.149
Na-perlargonate	25	-14 294	$18 \ 325$	0 058
Na-caprate	18	-15 997	24 364	0 020
Na-acid moloate	5	-7 461	6 868	0 001
Na-acid succinate	5	$8\ 216$	8 495	0.002
Na-acid adipate	07	3.755	4 515	0.001
K-acid malonate	5	-7 860	6 712	0 00 1
K-acid succinate	4.5	-8 322	8 1 45	0.003
K-acid adipate	1	-3 859	3 798	0 003

Table 4.1: (continued) Fit of the molality mean ionic activity coefficient data of pure aqueous uni-univalent electrolytes at 298.15K (Hamer and Wu, 1972)

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Table 4.2: Fit of the molality mean ionic activity coefficient data of pure aqueous non-uni-univalent electrolytes at 298.15 K. (Robinson and Stokes, 1959)

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Bi-Univalent Electrolyte	Max molality			Std Dev
1		λ_E	λ_W	of ln values
BaAc ₂	3 5	-7 896	8 499	0 072
BaBr ₂	2	-10 165	17 481	0 0 2 0
BaCl ₂	18	-10 230	16 172	0 021
$Ba(CLO_4)_2$	4	-8 759	14 128	0 029
Bal ₂	2	-10 259	20 725	0 015
CaBr ₂	6	-11 232	23 144	0 072
CaCl	10	-9 571	17 099	0 109
CaCl ₂	6	-10 474	19 052	0 021
Ca(CLO ₄) ₂	6	-10 383	22 683	0 005
Cal ₂	2	-10 533	23 061	0 007
$Ca(NO_3)_2$	6	-8 728	10 668	0 046
CdBr ₂	4	-14 308	16 558	0 365
$CdCl_2$	6	-12 640	11 085	0 333
CdI_2	2 5	-17 348	31 222	0 166
$Cd(NO_3)_2$	2 5	-8 970	13 166	0 023
CoBr ₂	5	-10 021	20 790	0 039
$CoCl_2$	4	-9 451	16 491	0 045
CoL	6	-10 190	$24\ 067$	0 100
Col ₂	5	-10 686	25 545	0 027
$Co(NO_3)_2$	5	-9 621	$16\ 256$	0.026
CuCl ₂	6	-6 977	8 941	0 048
$Cu(NO_3)_2$	6	-9 252	14 495	0 035
FeCl ₂	2	-10 565	19 608	0 019
MgAc ₂	4	-9 840	12 887	0 072
MgBr ₂	5	-10 967	$24\ 431$	0 025
MgCl ₂	5	-10 851	21 829	0 018
$Mg(ClO_1)_2$	4	-11 071	27 528	0 026
MgI ₂	5	-11 353	28.031	0 046
$Mg(NO_3)_2$	5	-9 686	1, 143	0 022
MnCl ₂	6	-7 921	12 0 44	0 067
N_1Cl_2	5	-9 649	17 326	0.052
$Pb(ClO_4)_2$	6	-9 492	$16\ 470$	0 028
$Pb(NO_3)_2$	2	-12 408	15 536	0 064
\mathbf{SrBr}_2	2	-10 623	20 372	0 013
SrCl_2	4	-10 134	17 316	0 020
$Sr(ClO_4)_2$	6	-9 668	18 944	0 042
SrI_2	2	-10 477	22 100	0 006
$Sr(NO_3)_2$	4	-8 977	9 426	0 041
$l O_2 Cl_2$	3	-8 559	15 159	0 024
$UO_2(CO_4)_2$	55	-11 626	33 720	0.029
$UO_2(NO_3)_2$	5 5	1 151	10 190	0 094
ZnBr ₂	6	-2 360	5999	0 058
ZnCl ₂	6	-8 255	9 2 1 9	0 029
Znl ₂	6	-1 888	7 525	0 149
$Zn(ClO_4)_2$	4	-11 372	28 689	0 0 1 9
$Zn(NO_3)_2$	6	-9 336	16 105	0 021

* Stables and Nuttall [124]
| Uni-Bivalent Electrolyte | Max molality | | <u> </u> | Std Dev |
|----------------------------------|--------------|-------------|-------------|--------------|
| | | λ_E | λu | of in values |
| Cs ₂ SO ₄ | 18 | -5 853 | 5 975 | 0.011 |
| K ₂ CrO ₄ | 3 5 | -7033 | 7 7 10 | 0 0 1 7 |
| K ₂ SO ₄ | 07 | -9 415 | 11 127 | 0 004 |
| L ₁₂ SO ₄ | 3 | -6 670 | 8 183 | 0.019 |
| Na ₂ CrO ₄ | 4 | -7 701 | 9 464 | 0.040 |
| Na ₂ -Fumarate | 2 | -7 089 | 10 096 | 0.004 |
| Na ₂ -Maleate | 3 | -8 990 | 11 278 | 0.027 |
| Na ₂ SO ₄ | 5 | -8 191 | 8 466 | 0.010 |
| $Na_2S_2O_3$ | 3 5 | -7 597 | 8644 | 0.021 |
| $(NH_4)_2SO_4$ | 4 | -8.378 | 8 327 | 0.022 |
| Rb_2SO_4 | 18 | -6 419 | 6.228 | 0.010 |
| H ₂ SO ₄ * | 75 | $-10\ 032$ | 11 436 | 0.232 |
| Bi-Bivalent Electrolyte | | | | |
| BeSO ₄ | 4 | -9 645 | 17 730 | 0.059 |
| MgSO ₄ | 3 | -9 870 | 17.529 | 0.052 |
| MnSO ₄ | 4 | -9 675 | 15622 | 0.051 |
| N1SO4 | 2.5 | -10 104 | 18.320 | 0.046 |
| CuSO ₁ | 1.4 | 11 415 | 24001 | 0.046 |
| ZnSO ₁ | 3 5 | -10 154 | 17 458 | 0.049 |
| CdSO₄ | 35 | -9 841 | 15 594 | 0.055 |
| UO ₂ SO ₄ | 6 | -8 853 | $13\ 29\ 4$ | 0.096 |
| Tri-Univalent Electrolyte | | | | |
| AlCl ₃ | 18 | -6 825 | 19 60 4 | 0.080 |
| CeCl ₃ | 2 | -4 237 | 12863 | 0.063 |
| $Co(en)_3Cl_3$ | 1 | -8 371 | 8 859 | 0.084 |
| CrCl ₃ | 12 | -1 171 | $13 \ 339$ | 0.073 |
| $Cr(NO_3)_3$ | 14 | -1.181 | 12176 | 0.070 |
| EuCl ₃ | 2 | -4 383 | 13541 | 0.068 |
| $Ga(ClO_4)_3$ | 2 | -6.863 | 25.722 | 0.158 |
| Tri-Univalent Electrolyte | | | | |
| $K_3Fe(CN)_6$ | 1 1 | -1 633 | 5 288 | 0.011 |
| LaCl ₃ | 2 | -4 250 | 12.874 | 0.063 |
| NdCl ₃ | 2 | -4 914 | 13 572 | 0.061 |
| PrCl ₃ | 2 | -4 465 | $13\ 002$ | 0.062 |
| ScCl ₃ | 18 | 3 346 | 13 837 | 0.059 |
| SmCl ₃ | 2 | -4 18 1 | $13 \ 452$ | 0.064 |
| YCl ₃ | 2 | -5 937 | 15,533 | 0.064 |
| Tri-Bivalent Electrolyte | | | | |
| $Al_2(SO_4)_3$ | 1 | 6 369 | 14 159 | 0.051 |
| $Cr_2(SO_4)_3$ | 1 2 | 0.687 | 11 116 | 0.132 |

Table 4.2: (continued) Fit of the molality mean ionic activity coefficient data of pure aqueous non-uni-univalent electrolytes at 298.15K (Robinson and Stokes, 1959)

***** Stables [123]

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to molality mean activity coefficient of aqueous solution of HCI at 298.15 K.



Figure 4.3: Experimental (Hamer and Wu, 1972) and calculated molality mean ionic activity coefficient of various uni-univalent electrolytes at 298.15 K.



Experimental values and values calculated with models other than the present study are those reported by Zemaites et al. (1986)



Figure 4.5: Molality mean activity coefficient of KOH by various models at 298.15 K.

Experimental values and values calculated with models other than the present study are those reported by Zemaites et al (1986)

5 00 $\square Ca(ClO_4)_2 (exp); \cdots Ca(ClO_4)_2 (calc)$ CaBr₂ (exp); CaB1 . (calc) CaCl₂(exp); -- CaCl₂(calc) 4 00 X $Cu(NO_3)_2$ (exp); - - $Cu(NO_3)_2$ (calc) ZnCl₂(exp); ---- ZnCl₂(calc) 3 00 2 00 $\ln(\gamma_{\pm})$ 1.00 0.00 -1 00 -2.00 0.00 2.00 4.00 6.00 MOLALITY

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Figure 4.6: Experimental (Stokes and Robinson, 1948) and calculated molality mean activity coefficient of various bi-univalent electrolytes at 298.15 K.

	Std. Dev. of ln values				
Electrolyte	Previous Work (1988)	This Work			
BeSO ₁	0.078	0.059			
MgSO ₁	0.074	0.052			
MnSO ₄	0.084	0.051			
NiSO ₄	0.072	0.046			
CuSO₄	0.067	0.046			
ZnSO ₄	0.083	0.049			
CdSO₄	0.073	0.055			
UO ₂ SO ₄	0.054	0 096			

Table 4.3: Comparison of fit for bi-bivalent electrolytes

and Na heptylate with good results. The standard deviation for H_2SO_4 for maximum molality 27.5 was 0.232.

For the study of temperature effects, the present model was used without any modification for various electrolytes at different temperature and model parameters were adjusted at each temperature. Table (4.4) shows the results of the fit for some salts at temperatures higher than 298 15K and Figure (4.7) presents the results for CaCl₂ at 474 K obtained using the various models. The average standard deviations for the salts shown in Table (4.5) are within 4.4 % for the present model while the standard deviation using Chen's model is 98 %. In Chen et al.'s model the interaction parameters are those evaluated at 298.15K and the temperature effect is introduced in parameter A of the Debye-Huckel expression. Contributions to the excess Gibbs energy due to long-range forces represented by the Debye-Hückel theory and to short-range forces represented by the NRTL-NRF model seem to be adequate in all the range from dilute solutions up to high ionic strengths. Figure (4.8) shows both contributions to the mole fraction activity coefficient of KOH in an aqueous solution. It is clear that long-range forces dominate at low ionic strength while short range forces dominate at high concentrations of electrolyte

In conclusion, the model presented in this work gives a realistic representation of aqueous solutions of a single electrolyte and can be used with confidence up to

Table 4.4: Fit of the molality mean ionic activity coefficient data of binary aqueous electrolyte mixtures at various temperatures.

	Max	Temperature			Std. Dev.
Electrolyte	Molality	(K)	λ_E	λW	of In values
HCI.	2	323 15	-8.366	12.563	0 002
KCI*	4	353.15	-8 541	9.452	0.008
КОН∗	17	353.1 5	-9.911	14.049	0 072
NaCl [†]	6	373.15	-8.760	10.599	0.017
NaCl [†]	6	573.15	-13.412	16.334	0 187
NaOH*	4	308 15	-8.361	10.620	0.011
MgSO ₄	2	350 15	-5 957	8 0 7 8	0 019
$Na_2SO_4^{\star}$	16	350.15	-9 639	11 709	0 021
$\mathrm{CaCl}_2^{\dagger}$	3.5	382 00	-8 459	14 260	0 015
$CaCl_2^1$	3.5	475 00	-10.315	14 233	0 092
MgCl [*]	2	353.15	-8 513	16.009	0.011

* Harned and Owen [65]

* Snipes et al. [119]

† Silvester and Pitzer [118]

‡ Holmes et al [72]

high ionic strengths.

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4.2.3 Optimization of the Binary Parameters

The model proposed in this work uses two binary adjustable parameters to fit the mean ionic activity coefficient data. The binary parameter, λ_E , is the difference of the dimensionless interaction energies between cation-anion pair and ion-molecule pair. The solvent parameter, λ_W , is the difference of dimensionless interaction energies between ion-solvent pair and solvent-solvent pair. These binary parameters presented in Tables (4.1), (4.2) and (4.3) were obtained by using the Powell algorithm [108] and minimizing the mean square standard deviation between the calculated and experimental mole fraction mean activity coefficients:

$$\sigma_{\gamma} = \left[\frac{\sum (\ln \gamma_{\pm}^{exp} - \ln \gamma_{\pm}^{calc})^2}{N}\right]^{1/2}$$
(4.63)

The results were converted to molality mean ionic activity coefficient as follows:





Experimental values and values calculated with models other than the present study are those reported by Zemaites et al (1986)



Figure 4.8: Long-range and short-range contributions on mean activity coefficient of aqueous solution of KOH at 298.15 K.

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		Std Dev of In Values of Activity Coefficient				
Electrolyte	Temp	Bromley	Meissner	Pitzer	Chen	Present Study
HCI	323 15	0 071	0.32	0 050	0.078	0.002
KCI	353 15	0 179	0 055	0 243	0 182	0 008
КОН	353 15	0 975	0 531	32 440	2 357	0 072
NaCl	373 15	0 266	0 169	0 274	0 154	0.017
NaCl	573 15	4 663	3 202	0 195	0 759	0 187
NaOH	308 15	0.096	0 098	0 0 3 8	0 095	0 011
MgSO4	350 15	0 851	0 279	0.038	0.060	0.019
Na_2SO_4	350 15	0 192	0 086	0.223	0 184	0 021
CaCl ₂	382 00	1 935	2 626	0.629	2.618	0.015
CaCl ₂	475 00	6 487	6 339	0.823	3 3 4 9	0 092
Avg Std Dev		1 602	1 342	3 495	0.981	0 0 14

Table 4.5: Comparison of models for electrolytes at various temperature (Zemaites et al., 1986).

$$\ln \gamma_{\pm}^{(m)} = \ln \gamma_{\pm} - \ln(1 + \frac{M\nu m}{1000})$$
(1.64)

The parameters were evaluated using the non-linear minimization algorithm proposed by Powell [108], program ZXPowell (International Mathematical and Statistical Library, 1975). Adjusting these two parameters presented some difficulties since both parameters are strongly correlated and in some cases the existence of multiple roots was found. As an example, two positive values, 12,173 and 11,938, were found for the parameters for LiClO₄ with standard deviation of 1.9% which is close to the value of 1.7% obtained with the parameters reported in Table (4.1). However for the sake of uniformity it was preferred to report the negative and positive values of the parameters, as shown in Tables (4.1) and (4.2). The only rationale for the above choice is that the opposite sign parameters gave the best fit of the data for almost all the systems studied.

Attempts were also carried out to determine the sensitivity of the results on the value assumed for the closest approach, B, in the Debye-Hückel model and on the coordination number Z in NRTL-NRF model. A value of 8 for Z and 1.2 for B yield the minimum value of standard deviation for majority of electrolytes. However, with

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B set to 2 for bi-univalent electrolytes the results improve significantly.

4.2.4 Activity Coefficients of the Ions

Activity coefficients of ions are not accessible to direct measurement. However using ionic solution theories, the mean ionic activity coefficient of an electrolyte can be reasonably separated into their ionic activity coefficients [13]. Although for aqueous solutions of a single electrolyte such as those considered in this work, eqs (4.60) and (4.61) suffice, for extension to multielectrolyte mixtures it would be desirable to have expressions for the individual ionic activity coefficients. These ionic activity coefficients are related to the mean ionic activity coefficient of the electrolyte as follows

$$(\nu_A + \nu_C) \ln \gamma^{\bullet}_{\pm} = \nu_A \ln \gamma^{\bullet}_A + \nu_C \ln \gamma^{\bullet}_C$$
(4.65)

Using electroneutrality, $Z_C \nu_C = Z_A \nu_A$, eq. (4.65) can also be written as

$$(Z_A + Z_C) \ln \gamma_{\pm}^* = Z_C \ln \gamma_A^* + Z_A \ln \gamma_C^*$$
(4.66)

As discussed by Prigogine and Defay [110], the condition of electroneutrality limits the possibility of knowing the values of all partial derivatives of the excess Gibbs energy. In fact, it is not possible to change the concentration of cations while keeping the concentration of anions constant and simultaneously maintaining the electroneutrality of the mixture. However, if we ignore the condition of electroneutrality and differentiate eq. (4.55) with respect to the number of moles of each individual ion we can obtain the activity coefficients of ions in the unsymmetrical convention. On the other hand, we are faced with an ambiguity when trying to derive expressions for the activity coefficients of ions because there are four different alternatives to use for the non-random factors Γ_E and Γ_W . One can write eq. (4.55) in its original form

$$\left(\frac{g^{ex}}{RT}\right)_{NRT\,L-NRF}^{*} = x_A x_C \lambda_E [Z_C(\Gamma_{CA} - 1) + Z_A(\Gamma_{AC} - 1)] - x_W^2(\Gamma_W - 1)\lambda_W$$

$$-x_c \ln \gamma_C^\infty - x_A \ln \gamma_A^\infty \tag{1.67}$$

where, according to eq. (4.40), Γ_{CA} and Γ_{AC} are equal. However, as one can see from eqs (4.38), (4.39) and (4.40) there are four different options which generate four different expressions for activity coefficients of ions. All of these expressions satisfy eq (4.65). Using the expressions given by eqs (4.38) and (4.39) for Γ_{4C} and Γ_{CA} results in two symmetrical expressions for the activity coefficients of ions which have the same values for uni-univalent electrolyte solutions. However, using only one of the eqs (4.38) or (4.39) for both Γ_{4C} and Γ_{CA} , as suggested by eq. (4.40), results in different values for the activity coefficients of ions for a uni-univalent electrolyte mixture. By investigating the different options, it was found that the following expressions for non-random factors yield values for activity coefficients of the ionic species which are different and comparable to the values obtained from the hydration model [15].

$$\Gamma_E = \Gamma_{CA} = \Gamma_{4C} = \frac{\beta_E}{x_W + Z_C x_C \beta_E} \tag{4.68}$$

$$\Gamma_{W} = \frac{1}{x_{W} + (Z_{A}x_{A} + Z_{C}x_{C})\beta_{W}}$$
(4.69)

using eqs (4.68) and (4.69), one can differentiate eq. (4.67) with respect to the number of moles of ions to obtain the following expressions for the individual activity coefficients of ions.

$$(\ln \gamma_{C}^{*})_{NRTL-NRF} = (Z_{A} + Z_{C})x_{A}(x_{W} + x_{A})(\Gamma_{E} - 1)\lambda_{E} + (Z_{A} + Z_{C})x_{A}x_{C}(x_{W}\frac{1 - Z_{C}\beta_{E}}{\beta_{E}} + Z_{C}x_{A})\Gamma_{E}^{2}\lambda_{E} + x_{W}^{2}(\Gamma_{W} - 1)\lambda_{W} - (1 - Z_{c}\beta_{W})(x_{W}^{3}\Gamma_{W}^{2} - 1)\lambda_{W} - x_{A}x_{W}^{2}\beta_{W}(Z_{A} - Z_{C})\Gamma_{W}^{2}\lambda_{W}$$

$$(4.70)$$

$$(\ln \gamma_A^*)_{NRIL-NRF} = (Z_A + Z_C) x_C (x_W + x_C) (\Gamma_E - 1) \lambda_E + (Z_A + Z_C) x_A x_C (x_W \frac{x_W}{\beta_E} + Z_C x_C) \Gamma_E^2 \lambda_E + x_W^2 (\Gamma_W - 1) \lambda_W - (1 - Z_A \beta_W) (x_W^3 \Gamma_W^2 - 1) \lambda_W - x_C x_W^2 \beta_W (Z_C - Z_A) \Gamma_W^2 \lambda_W$$

$$(4.71)$$

Notably, eqs (4.70), (4.71) and (4.60) satisfy eq (4.65). Thus, in spite of their mathematical shortcomings, eqs (4.70) and (4.71) may be used together with the long-range contribution presented in Chapter 3, eq. (3.9), to obtain the activity coefficient of individual ions as,

$$\ln \gamma_{i} = (\ln \gamma_{i})_{DH} + (\ln \gamma_{i}^{*})_{NRTL-NRF}$$

$$(4.72)$$

Table 4.6: Activity coefficients of ionic species in aqueous solutions of NaCl at 298.15K

[]	$\gamma(\mathrm{Na^+})$		γ(Cl ⁻)		
	Hydration	NRTL-NRF	Hydration	NRTL-NRF	
Molahty	Model	Model	Model	Model	
01	0 783	0 771	0 773	0 771	
02	0 744	0 725	0 726	0 723	
05	0 701	0 674	0 661	0 667	
10	0 697	0 662	0 620	0 637	
20	0 756	0 721	0 590	0 625	
3.0	0 870	0 839	0 586	0 626	
40	1.038	1 010	0 591	0 627	
50	1 272	1 239	0 600	0 624	
60	1 594	1 535	0 610	0 617	

As one can see from Table (4.6), the calculated activity coefficients of ions for binary aqueous solutions of NaCl are very close to the values obtained by the hydration

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model [15]. This agreement is surprising since both models are quite different in nature. Should a strong disagreement had been found it would have been difficult, without further experimental evidence, to decide which model gave more realistic values.

4.3 Synopsis

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Recent models for the estimation of the mean ionic activity coefficient of electrolytes in aqueous solutions (Cruz and Renon [36]; Chen el al [30,31]) have made use of variations of the NRTL model [114] for the excess Gibbs energy of a liqted mixture. Thus, these models for electrolyte solutions include the following basic assumptions of the NRTL approach.

- 1. Solution considered to consist of different types of cells which depend on the central species.
- 2. The contribution of each cell to the excess Gibbs energy of the mixture is the difference between the Gibbs energy of the cell and that of a hypothetical cell of pure central species

with these assumptions, the two-parameter models based on NRTL produce satisfactory results up to a concentration of six molal for solutions of a single electrolyte but the predicted results rapidly deviate from experiment at higher molalities

In this work a new local composition model is developed. Long-range interactions are accounted for by the Debye-Hückel theory. Local compositions, expressed in terms of non-random factors, are used to represent the effect of short-range interactions in aqueous electrolyte solutions. While the assumption of the existence of different types of cells, dependent on their central species, has been retained, the contribution to the excess Gibbs energy from each type of cell is treated differently from previous NRTL models. In agreement with the concept of non-random factors, the contribution to the excess Gibbs energy from each cell has been expressed by the difference between the Gibbs energy of the cell and that of a cell with the same central particle in a random mixture. The new two-parameter model is able to correlate the mean ionic activity coefficient of electrolytes in aqueous solutions from the dilute region up to saturation. The empirical Wilson-type expression [135] used in this work to represent the non-random factors has all the theoretical limitations and practical advantages of similar expressions used in NRTL-type treatments [130]. The two-parameter model obtained in this work with the non-random factor interpretation of the local composition concept is the best two-parameter model available for aqueous solutions of single electrolytes.

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Chapter 5

Experimental Techniques for the Measurement of Mean Ionic Activity Coefficients in Aqueous Electrolyte Solutions

5.1 Introduction

For more than a century, different techniques have been used to measure thermodynamic properties of electrolyte solutions. One of the most important functions in phase equilibria is the excess Gibbs energy in terms of temperature and composition. In fact, the excess Gibbs energy is a function from which other thermodynamic properties such as activity coefficients or heats of mixing can be obtained. In practice the excess Gibbs energy is not directly measurable and it is evaluated from a knowledge of the activity coefficients of the components in a mixture. Moreover, in binary solutions of an electrolyte and a solvent, the mean ionic activity coefficient of the electrolyte can not be directly measured and must be evaluated indirectly from the fugacity of the solvent or back calculated from measurement of the potential in electrochemical cells

For ternary systems the evaluation of mean ionic activity coefficients is even more difficult than in binary systems. In the following paragraph we discuss an important feature of electrolyte systems and then we briefly review the different experimental techniques for the evaluation of mean ionic activity coefficients in binary systems.

In the first place, as indicated by Pitzer [103] " because of space- charge effects, single-ion activity coefficients are not measurable by ordinary thermodynamic methods. Ultrasensetive methods measuring individual ions may make such quantities measurable in the future" On the other hand, although not attainable through direct measurements, activity coefficients of individual ionic species appear in many formulations of thermodynamic relations. In addition it is sometimes useful to postulate mathematical models to compute them for complex mixtures because these values can be easily combined to obtain mean activity coefficients for electrolytes in the mixture. In Chapter 4, a mathematical method for calculating the activity coefficient of individual ions was presented.

According to the Phase Rule (F=N-r s- π +2) [122], when one non-volatile salt is dissolved in degassed water at a given temperature and the two-phase system $(\pi=2)$ is allowed to reach equilibrium, we have two degrees of freedom. The salt and its ions plus water are four chemical species (N=4) related by one chemical equilibria (r=1)and with a fixed ratio of ions (s=1). In fact, if one ignores the ionic dissociation and considers only the salt and molecular water, the number of degrees of freedom from the phase rule is the same as above. Therefore the intensive equilibrium state of a binary electrolyte system can be characterized by the specification of two independent intensive variables. The measurable intensive variables of interest are pressure, temperature and composition Thus for a binary electrolyte system in which vapor is pure solvent, measurements of the activity of solvent as a function of composition at a given temperature permits the calculation of the activity of the electrolyte by the use of the Gibbs-Duhem equation. The intensive equilibrium state of a single-phase two-components system is determined by the specification of three independent intensive variables. Measuring more variables leads to over determination of the system and makes it possible to use the Gibbs-Duhem equation to check for thermodynamic consistency. Conversely, in a single phase binary mixture a knowledge of the mean

ionic activity coefficient of the salt as a function of composition at a given temperature and pressure allows the calculation of the activity coefficient of the solvent by the use of the Gibbs-Duhem equation.

5.2 Experimental Methods

Generally two methods are widely used to measure the activity coefficients of nonvolatile electrolytes in solution. These are solvent activity methods and electrochemical cell techniques. In solvent activity methods, one first calculates the activity coefficient of the solvent by measuring the equilibrium pressure of the pure solvent vapor phase with the binary mixture and then using the Gibbs-Duhem equation to calculate the mean ionic activity coefficient of the electrolyte. The second method allows a direct calculation of the activity of an electrolyte by measurement of the electrochemical potential of ions in an electrochemical cell. Wilhort [134] has presented a useful review of experimental techniques that have been widely used during the last fifty years

5.2.1 Solvent Activity Methods

Solvent activity or vapor pressure method has been traditionally used in vapor-liquid equilibria studies of aqueous electrolytes. Different techniques have been proposed [116] depending on the way of measuring the activity of the solvent. The most widely used methods are the static and the isopiestic method.

5.2.1.1 The Static Method

Static methods are easy to use for mixtures in which one component is non-volatile, as in the case, for instance, of polymer solutions or some electrolyte solutions. Due to the lack of volatility of one component, the vapor phase consists entirely of the volatile solvent and there is no need to obtain a sample for analysis of the equilibrium compositions. In this case, the composition of the liquid phase can be evaluated from a mass balance of the total amounts of the two components in the system, the vapor pressure and the vapor volume. The use of a pressure transducer permits the monitoring of the vapor pressure of solvent at various temperatures. The most cumbersome step in the static method is the complete elimination of all air from the system. The static method is particularly useful for binary electrolyte solutions [4,116].

5.2.1.2 The Isopiestic Method

This technique was introduced by Bousfield in 1918 [116] and improved by Sinclair [116]. The mean ionic activity coefficients of several hundred single-salt aqueous solutions and their free energies of mixing have so far been determined by means of the isopiestic method [64,65,100,116]. It is a comparative method which uses two solutions of different electrolytes with the same solvent. An open dish of the solution under investigation is placed in a sealed vessel along with a similar dish of a reference solution, whose solvent activity is known as a function of concentration. The solvent distills isothermally from one dish to another until its chemical potential is the same in each solution. Due to equality of chemical potential of the solvent in all solutions at equilibrium, it is convenient to choose the same standard state for the solvent in all solutions. When this is, the case, the solvent activity over both solutions will also be the same. From a series of measurements at various molalities one can construct a cuive of the isopiestic ratio against the molality of either electrolyte. The isopiestic ratio is defined by

$$\boldsymbol{R} = \frac{\nu_R m_R}{\nu_X m_X} \tag{5.1}$$

where m_X and m_R are the molalities of the measured and the reference samples respectively and, ν_X and ν_R are the corresponding total stoichiometric numbers. It is usual to express the solvent activity by means of the practical osmotic coefficient. This is a function that expresses the deviation from ideality of the solvent in a more pronounced way than the activity of the solvent, a_S

$$\phi = \frac{-\frac{1000}{M} \ln a_S}{\Sigma \nu_i m_i} \tag{5.2}$$

where M is the molecular weight of the solvent. In terms of the osmotic coefficient, the condition of equal activity (vapor pressure) is given by

$$\nu_R m_R \phi_R = \nu_X m_X \phi_X$$

or

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$$\phi_X = \boldsymbol{R} \ \phi_R \tag{5.3}$$

thus ϕ_X can be obtained from **R** and ϕ_R .

As discussed in Chapter 2, from ϕ_X the mean ionic activity coefficient γ_{\pm} can be calculated using the integrated Gibbs-Duhem equation:

$$-\ln \gamma_{\pm X} = (1 - \phi_X) + \int_0^m (1 - \phi_X) d \ln m_X$$
 (5.1)

Alternatively if **R** and $\gamma_{\pm R}$ are available, one can use the following relation [116].

$$\ln \gamma_{\pm X} = \ln \gamma_{\pm R} + \ln R + \int_0^{m_X} (R - 1) d \ln(\gamma_{\pm R} m_{\pm R})$$
(5.5)

Although the isopiestic method provides a simple and convenient way of measuring the activity of the solvent, it suffers from two main drawbacks. The attainment of equilibrium needs a great deal of skill and it can take several days to obtain reliable data. For example, the time required for a 0.1 m solution to reach equilibrium is three to four days and therefore this technique is inappropriate at very low concentrations. Another disadvantage is that this technique is cumbersome to use for multicomponent electrolyte solutions

McKay and Perring [90] have proposed an isoplestic method for multicomponent mixtures. Even when reliable data are obtained for the osmotic coefficient of the solvent, the mean ionic activity coefficients of the individual salts can not be obtained easily.

5.2.2 Electrochemical Methods

Electrochemical cells are an essential tool for experimental studies of electrolyte solutions and have been used widely in electrochemistry for measurement of thermodynamics properties of electrolyte solutions. In contrast to vapor pressure measurements, this technique is very useful for the measurement of the chemical potential or activity of electrolytes in very dilute binary electrolyte mixtures. One can directly determine the activity of salts in aqueous electrolyte mixtures. Thus this technique provides an independent check on the validity of the thermodynamics relation used to calculate the electrolyte activity from solvent activity methods. Many experimental data for binary aqueous electrolyte solutions have been measured using this method. This technique can be adapted for multicomponent solutions provided that each electrade is selective only to one specific ion. Mean ionic activity coefficients for ternary systems with common ions have been reported in the literature [14,22,83,128]. To the best of this author's knowledge very few data have been reported for ternary systems without a common ion. In the last decade ion-selective electrodes have been used in industry and in research to measure specific ion concentrations, activity of electrolytes and the pH of solutions. In this section we will discuss the basic principles and equations governing electrochemical cells and the potentiometric technique.

5.2.2.1 Electrochemical Cells

An electrochemical cell consists of two conductors or electrodes immersed in a single electrolyte solution, or of two different solutions in electrical contact. Electrochemical cells may be divided into two categories. The first one consists of galvanic cells which convert chemical energy into electrical energy by an oxidation-reduction reaction. The others are the electrolytic cells which are used to carry out chemical reactions at the expense of electrical energy. In an electrochemical cell the electrochemical potential of species i in phase α may be written as

$$\bar{\mu}_{i}^{\alpha} = \mu_{i}^{\theta\alpha} + RT \ln a_{i}^{\alpha} + Z_{i}F\phi_{i}^{\alpha}$$
(5.6)

where $\mu_i^{\theta\alpha}$ and a_i^{α} are the standard chemical potential and activity of species *i* in phase α respectively. Z_i is the charge number of species *i*, *F* is the Faraday constant (96,485 coulombs/mole) and ϕ^{α} is the potential in phase α . Equation (5.6) can be written for phase β as:

$$\bar{\mu}_{i}^{\beta} = \mu_{i}^{\theta\beta} + RT \ln a_{i}^{\beta} - Z_{i}F\phi_{i}^{\beta}$$
(5.7)

At equilibrium the electrochemical potential of species i should be the same in phases α and β .

$$\bar{\mu}_{i}^{\alpha} = \bar{\mu}_{i}^{\beta}$$

so that

$$\mu_i^{\alpha} - \mu_i^{\beta} = Z_i F E \tag{5.8}$$

where

$$\mu_i^{\alpha} = \mu_i^{\theta \alpha} + RT \ln a_i^{\alpha} \tag{5.9}$$

$$\mu_{i}^{\beta} = \mu_{i}^{\theta\beta} + RT \ln a_{i}^{\beta}$$
(5.10)

$$E = \phi_i^{\alpha} - \phi_i^{\beta} \tag{5.11}$$

Using eq. (5.8) the molar change of the Gibbs energy of the reaction can be written as:

$$\Delta g_{i} = -Z_{i}FE \tag{5.12}$$

Equation (5.12) is the starting point of the study of electrochemistry [11,47,80]. For example, in a reduction-oxidation reaction for a uni-univalent electrolyte, the molar Gibbs energy of the reaction can be written in terms of eq. (5.12) so that the classical Nernst equation is obtained as [27]

$$E = E^{\circ} - \frac{RT}{ZF} \ln(m_C m_A \gamma_{\pm}^2)$$
(5.13)

 E° is the standard electrochemical potential of the standard oxidation-reduction reaction in which all the reactants and products are in their unit activity standard state. The molalities of the cation and anion are m_C and m_A , respectively. The most common form of the Nernst equation used by electrochemists, at 298.15 K, is of the form:

$$E = E^{\circ} - \frac{0.05916}{Z} \log(m_C m_A \gamma_{\pm}^2) \quad (in \ volts)$$
 (5.14)

In electrochemistry, potentiometry is the appropriate tool to use in obtaining chemical information, such as the activity of salts, by measurement of cell voltages. To set up an electrochemical cell to determine the activity of an electrolyte in an aqueous solution, usually one needs at least two half-cell electrodes to insert into the solution. One of these electrodes, which responds directly to the analyte, is called the indicator electrode. The other electrode, against which the potential of analyte should be compared, is called the reference electrode. One of the most advanced types of indicator electrodes are the Ion-Selective Electrodes (ISE). These are widely used for the determination of mean ionic activity coefficients of electrolytes in binary and in ternary aqueous electrolyte systems.

5.2.2.2 Ion-Selective Electrodes (ISE)

In electrochemistry the hydrogen electrode, which consists of platinum and hydrogen gas, is used as a reference electrode. The potential of all types of electrodes are measured with respect to the H₂-electrode whose potential is arbitrarily set to zero. In addition to H₂-electrodes and pure metal conductors (first kind electrodes), three

different types of electrodes are constructed by manufacturers. These are electrodes of the second kind, electrodes of the third kind and ISE. In this review we do not intend to elaborate and explain the construction and design of all electrodes, however we will briefly describe some basic aspects of reference and ion selective electrodes which we have used in our measurements. For more details, other references [27,47,80] can be consulted.

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Most of the electrodes consist of a pure metal part such as silver (Ag) and some other material. For example, an electrode of the second kind is a metal conductor coated with a thin layer of one of its slightly soluble anion salts (Ag,'AgCl). Ion-Selective Electrodes are electrochemical half-cells in which a potential difference, dependent on the activity of a particular ion in solution, arises across the electrode/electrolyte interface. Ion-selective Electrodes, as the name indicates, respond selectively to a particular ion in the presence of others. Ion-Selective Electrodes are now commercially available for about twenty common anions and cations and they can be classified in the four following groups [44,47,80]: 1) glass electrodes, 2) solid state electrodes, 3) liquid membrane electrodes and 4) gas and enzyme electrodes.

The sensitive part of an ISE is a membrane which is in contact with the sample solution. The membranes are semi-permeable so that only one kind of ions (ions of the same sign) may be selected. The mechanism of the ion selectivity depends on the type of ISE. The most common and oldest ISE's are the glass electrodes. The pH glass electrode is one of the most important examples of glass electrodes used in the laboratory. Other glass electrodes, such as those for sodium and armonium, are widely used in the determination of the activity of Na and NH₄ ions. Solid-state electrodes are based on inorganic salt crystals. The membrane of these ISE's comprises of "a non-porous layer of a sparingly soluble salt in contact with a solution containing a single kind of ion. Another kind of ion then constitutes the charge carrier within the membrane. Membranes made of silver halides serve as an example. The membrane potential depends on the anion activity in the solution, and Ag⁺ is the charge carrier in the membrane" [27,47,80]. Examples of these type of electrodes include Cl^- , Br^- , F^- and I^- .

Liquid membrane electrodes are based on a hydrophobic membrane saturated with a hydrophobic liquid ion exchanger [66,80]. The ion exchange material is sup-

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ported by a solid plastic membrane. The sensed ion is exchanged across the membrane creating a potential which contributes to the total potential of the ISE. While solid state electrodes respond to monovalent anions and glass electrodes respond to certain monovalent cations, only liquid membrane electrodes respond to some of important ions such as NO_3^- , Ca^{24} and K^+ . Gas electrodes are used for estimation of the solubility of CO_2 and NH_3 in solutions.

5.2.2.3 Reference Electrodes

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The signal of an ion-selective electrode needs to be measured against a reference electrode. In other words, a reference electrode is a half cell electrode which provides the second terminal of an electrochemical cell. The reference electrode should maintain a constant potential relative to the sample solution, regardless of its composition and should not cause chemical changes in the solution. Reference electrodes can be grouped in two classes depending on whether they operate with or without a liquid junction. The three most common liquid junction reference electrodes are (I) silver chloride (II) mercury chloride (calomel) and (III) mercury sulphate. We only show the silver-chloride reference electrode here. The silver chloride reference electrode is the most common reference electrode in current use. It can be represented by

KCl(satd), AgCl(satd)/Ag(s)

Figure (5.1) shows a single junction reference electrode. It consists of a silver wire coated with AgCl in contact with an internal filling solution of saturated KCl. This solution contains Cl^- ions of a fixed activity which keeps the potential of the reference electrode constant. The internal solution is in contact with the sample solution through a porous plug or a flow restriction which permits the filling solution to flow very slowly into the sample. This kind of reference electrodes are called single junction electrodes. The half cell reaction is

$$AgCl(s) + e \rightleftharpoons Ag(s) + Cl^{-}$$



Figure 5.1: Schematic view of a Single Junction Reference Electrode and the half cell potential is written as:

$$E_{Ref} = E^o_{AgCl/Ag} - \frac{RT}{F} \ln a(Cl^-)$$
(5.15)

One of the major reasons for drift in reference electrodes is that some interfering species may diffuse across the porous plug from the solution under investigation into the internal solution [47,80]. A second liquid junction enables contact to be made between the internal filling solution and the sample so that interfering of ions from the sample solution to internal solution may be prevented. This type of electrode with two salt bridges is called a double liquid junction reference electrode [27,47].

Salt bridge solutions should be compatible with sample solutions. It is desirable that salt bridge solutions should be equitransferent, *i.e.*, that the transport numbers of its anions and cations should be nearly equal. This condition minimizes the liquid junction potential, which can otherwise drift and cause instability.

As indicated by Kakabadse [74] "An elegant way of overcoming liquid-junction potential is to use one ion-selective electrode as a reference electrode for another." This type of measurements need a dual differential electrometer so that the signal of one ISE can be measured respect to another ISE. In the next chapter, a description of how an Orion milivoltmeter was used to monitor the signal of one ISE towards another ISE in ternary electrolyte systems is provided.

5.2.2.4 Potential of an Ion-Selective Electrode

As shown in Figure (5.2) an Ion-Selective Electrode usually consists of a secondary type electrode (Ag/AgCl) immersed in a standard filling solution which is in contact with a sample solution through a semi-permeable membrane. Two processes control the membrane potential of an ISE [47,80]. The first is the diffusion of ions through the membrane in a liquid-membrane electrode or a floride ISE, the second is the ion exchange reactions at the membrane boundary in solid state and glass electrodes. As shown in Figure (5.3) the membrane is in contact with two electrolyte solutions, the sample solution and the standard solution. The potential of an ion-selective electrode for a specific ion may be obtained from the following relation [80,116,120].

$$E_{ISE} = E_R + \Delta E + E_{ASY} \tag{5.16}$$

Where E_R is the potential of the internal reference electrode (Ag/AgCl), ΔE is the membrane potential and E_{ASY} is an asymmetric potential of the electrode. The potential of the internal reference electrode, which consists of an Ag wire coated with AgCl may be written as:

$$E_{R} = E^{o}_{Ag/AgCl} - \frac{RT}{F} \ln a(Cl^{-})$$
(5.17)

The activity of Cl⁻ in the internal solution of a reference electrode and in the standard internal solution of an ISE are different, thus E_{Ref} and E_R are usually different. The major contribution to the potential of an ISE is the membrane potential (ΔE) which depends on the type of ISE. Most membranes are made from solid crystals



Figure 5.2: Schematic view of a chloride Ion Selective Electrode (ISE)

or organic liquids embedded on a solid support. They have fixed active sites or mobile active sites, on both sides, in contact with both inner and outer electrolyte solutions. They are thick enough to have an interior region of unique composition with respect to the solutions outside [47,80]. The way in which the membrane works depends on the type of ISE. However, the phenomena occurring at the interface between two electrolytes are a diffusion process and a Donnan equilibria [11,78,80]. The membrane potential is the result of the diffusion potential and the Donnan potential. "The diffusion potential, which is reflected in the liquid junction potential, results from the different mobilities and concentrations of the ions in the electrolytes in contact while the Donnan potential is due to the transfer of one or more kinds of ions across the interface between two electrolytes." [80] Thus as shown in Fig (5.3), ΔE is the difference in the potential of a specific ion in the inner solution (2) and outer solution (1).

$$\Delta E = E_1 - E_2 \tag{5.18}$$



Figure 5.3: Membrane of an Ion Selective Electrode

The terms E_1 and E_2 are called the inner-potential of the phases (1) and (2), respectively.

To a first approximation, one can assume the ISE is selective only to one specific ion so that no interferences from other ions are observed. In addition one can assume that the membrane has the same number of fixed sites on both boundary surfaces. Following these assumptions and using the relations for the electrochemical potential of ions and the boundary ion exchange relations, one can obtain the membrane potential for a specific ion i as [47,120]:

$$\Delta E = E_1 - E_2 = \pm \frac{RT}{Z_1 F} \ln \frac{a_1(1)}{a_1(2)}$$
(5.19)

However the membrane potential of an actual ISE is not given by a relation as simple as equation (5.19). In fact ISE's are permselective, *i.e.*, they have selectivity towards other ions of the same sign as the ion of interest in the solution Based on more realistic assumptions the membrane potential of an ISE can be written as [78,80,120]:

$$\Delta E = E_1 - E_2 = \pm \frac{RT}{Z_i F} \ln \frac{a_i(1) + \sum_j K_{ij}^{pot} a_j^{Z_i/Z_j}(1)}{a_i(2)}$$
(5.20)

Where K_{ij}^{pot} is the selectivity coefficient of the ISE, which is selective to ion *i*, towards ion *j*.

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$$K_{ij}^{pot} = \frac{\text{response to } j}{\text{response to } i}$$

 K_{ij}^{pot} is not an empirical coefficient, but arises from a consideration of the diffusion process and of the Donnan equilibria. In general it can be obtained as [78,120]:

$$K_{ij}^{pot} = \left| \frac{U_j}{U_i} \right| K_{ij} \tag{5.21}$$

where U_j and U_i are the mobilities, within the electrode membrane, of ion j and i respectively. The factor K_{ij} is the equilibrium constant for the Donnan reaction. Eq. (5.20) for a ternary aqueous electrolyte solution can be written as:

$$\Delta E = E_1 - E_2 = \pm \frac{RT}{Z_1 F} \ln \frac{a_1(1) + K_{12}^{Pot} a_2^{Z_1/Z_2}(1)}{a_1(2)}$$
(5.22)

Substituting eq. (5.22) in eq. (5.16).

$$E_{ISE} = E' \pm \frac{RT}{Z_1 F} \ln \left[a_1(1) + K_{12}^{Pot} a_2^{Z_1/Z_2}(1) \right]$$
(5.23)

where

$$E' = E_R + E_{ASY} \mp \frac{RT}{Z_1 F} \ln a_1(2)$$
(5.24)

The asymmetry potential E_{ASY} of the ISE depends on the crystal structure of the electrode body, particularly in glass ISE's.

Eq. (5.23) is called Nikolsky-Eisenman equation and was proposed to approximate the effect of the interfering ions. The selectivity coefficient K_{12}^{pot} is usually obtained experimentally using various methods which will be discussed in the next section. As is evident from eq. (5.24), E' is the electromotive force (emf) of the measuring circuit with a standard internal solution and depends on the activity of ions in the inner solution and the type of internal reference electrode. The theoretical value of RT/F at 298.15 K is 25.692 mv. This is the slope of an ISE in the case of Nernstian behavior when the natural logarithm is used for the activity of the ions.

5.2.2.5 The Electromotive Force of an Electrochemical Cell

An electrochemical cell for potentiometric measurements is usually set up as shown in Fig (5.4). The electromotive force of the cell 1s given by

$$E = E_{ISE} - E_{Ref} + E_j \tag{5.25}$$

Where E_{Ref} is the potential of the reference electrode and E_j is the liquid-junction potential of the reference electrode. Substituting eq. (5.23) in (5.25):

$$E = E' \pm \frac{RT}{Z_1 F} \ln (a_1 + K_{12}^{pot} a_2^{Z_1/Z_2}) - E_{Ref} + E_j$$

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$$E = E'_{cell} \pm \frac{RT}{Z_1 F} \ln\left(a_1 + K_{12}^{pot} a_2^{Z_1/Z_2}\right)$$
(5.26)

where

$$E'_{cell} = E_R - E_{Ref} + E_j + E_{ASY} \mp \frac{RT}{Z_1 F} \ln a_1(2)$$

and the sign + is for a cation and the sign - is for an anion.

5.2.2.6 Determination of the Activity of an Electrolyte using ISE's

The activity of an electrolyte which consists of cation C and anion A may be obtained by two alternative methods. The first method is to measure the emf of both cation ISE and anion ISE towards a single junction or double junction reference electrode and then subtract the two values to get the activity of the salt [27,47]. Thus eqs (5.25) and (5.26) can be written, for both ISE's, as



Figure 5.4: Schematic view of an electrochemical cell

$$E(1) = (E_R^C - E_{Ref} + E_j + E_{ASY}^C) - \frac{RT}{Z_C F} \ln a_C(2) + \frac{RT}{Z_C F} \ln a_C$$
$$E(2) = (E_R^A - E_{Ref} - E_j + E_{ASY}^A) + \frac{RT}{Z_A F} \ln a_A(2) - \frac{RT}{Z_A F} \ln a_A$$

from which

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$$E = E(1) - E(2) = (E_R^C - E_R^A) + (E_{ASY}^C - E_{ASY}^A) - \frac{RT}{F} \ln a_C^{1/Z_C}(2) a_A^{1/Z_A}(2) + \frac{RT}{F} \ln a_C^{1/Z_C} a_A^{1/Z_A}$$
(5.27)

The other alternative [74,128] is to use the anion ISE as a reference electrode as follows,

$$E = E_{ISE}^{C} - E(\text{reference}) = E_{ISE}^{C} - E_{ISE}^{A}$$

and, using eqs (5.23) and (5.24)

$$E = (E_R^C - E_R^A) + (E_{ASY}^C - E_{ASY}^A) - \frac{RT}{F} \ln a_C^{1/Z_C} (2) a_A^{1/Z_A} (2) + \frac{RT}{F} \ln a_C^{1/Z_C} a_A^{1/Z}$$
(5.28)

The first treatment is available in the literature [47,35] with a different nomenclature. In this work we have written the equations for second treatment in a way which allows us to show that both methods are equivalent. As one can see from eqs (5.27) and (5.28) both methods give the same result. Equation (5.28) can be written for uni-univalent salts as

$$E = E' + S \ln a_{CA} \tag{5.29}$$

where:

$$E' = (E_R^C - E_R^A) + (E_{ASY}^C - E_{ASY}^A) - S \ln a_{CA}(2)$$

$$a_{CA} = a_C a_A = \text{activity of the salt}$$
(5.30)

S = slope of electrode

As will be discussed in the next chapter, in experiments in this study the emf of cation ISE towards an anion ISE was monitored, so that E' and S were obtained experimentally. As mentioned before, S is equal to RT/F for a Nernstian response of the ISE's. In this experimental work both methods were used, *i.e.*, both single and double junction reference electrodes and ISE as a reference electrodes. The important

advantage which can be obtained by the use of ISE's as reference electrodes is to eliminate the liquid junction potential which is associated with reference electrodes and results in emf drift [47,80].

5.2.2.7 Determination of the Selectivity Coefficient of an ISE

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Different methods have been proposed [27,41,54,70,88,131] to determine the selectivity coefficient (K_{ij}^{pot}) of ISE's. Among these methods, two of them have been widely used. These are the separate-solution technique and the mixed-solution technique [111]. In the mixed solution method, the value of K_{ij}^{pot} is usually obtained by measuring the response of an ISE in the presence of both the measuring ion and the interfering ion. However in order to apply this method one must have the activity coefficient of the individual ions in the mixture. The mixed solution method is particularly useful for very dilute solutions because the activity coefficients of the ions can be calculated using the Debye-Hückel Theory. Jince our experiments are at high concentration, we will describe only the separate solution method [27,111]. The separate solution method is based on two emf measurements performed by introducing an iSE which is selective forwards an ion i into both a solution containing the primary ion i at activity a_i , $(E_i)_{soli}$ and a solution containing the interfering ion j at activity a_j , $(E_i)_{sol j}$. Figure (5.5) shows the calibration curves for both solutions. For the measured ion i in both solutions containing ions i and j, the Nikolsky-Eisenman equation can be written as

$$(E_{i})_{soli} = E'_{i} + \frac{S}{Z_{i}} \ln(a_{i})$$
(5.31)

$$(E_{i})_{sol,j} = E'_{i} + \frac{S}{Z_{i}} \ln(K^{pot}_{ij} a^{Z_{i}/Z_{j}}_{j})$$
(5.32)

Subtracting equation (5.31) from (5.32):

$$(E_{i})_{sol.j} - (E_{i})_{sol.i} = \frac{S}{Z_{i}} \ln \frac{a_{j}^{Z_{i}/Z_{j}}}{a_{i}} + \frac{S}{Z_{i}} \ln K_{ij}^{pot}$$



Figure 5.5: Calibration lines for determining the selectivity coefficient of ISE's by the separate solution method

and rearranging

$$\ln K_{ij}^{pot} = \frac{(E_i)_{sol j} - (E_i)_{sol i}}{S/Z_i} - \ln \frac{a_j^{Z_i/Z_j}}{a_i}$$
(5.33)

Equation (5.33) may be used to evaluate the selectivity coefficient. However as shown in Fig (5.5) two alternatives can be applied for determining the selectivity coefficient [111,131]. The first alternative is called "the equal activity method" [111, 131]. According to the equal activity method, the emf of an ISE is obtained at the same activities of the primary ion i and interfering ion j. Since

 $a_i = a_j = a^*$

then, from eq. (5.33):
$$K_{ij}^{pot} = \frac{1}{a^{(Z_i/Z_j-1)}} exp[\frac{(E_i)_{sol,j} - (E_i)_{sol,i}}{S/Z_i}]$$
(5.34)

The other alternative is called "the equal potential method" [111,131]. According to this method, as shown in Fig (5.5), K_{ij}^{pot} is evaluated by using the measured and interfering ion activities which give rise to the same signal.

$$(E_i)_{sol.i} = (E_i)_{sol.j}$$

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and, from eq. (5.33)

$$K_{ij}^{pot} = \frac{a_i}{a_j^{Z_i/Z_j}}$$
(5.35)

A special case is the series of solid state or single crystal ISE's. These are precipitate based electrodes in which only surface exchange reactions can take place. Then, the potential selectivity coefficient for this type of ISE's may be theoretically calculated from the equilibrium constant of the ion-exchange reaction at the surface, *i.e.*,

$$K_{ij}^{pot} = K_{ij}$$

 K_{ij} may be obtained as the ratio of the solubility products of the electrode material (K_{i}^{sp}) to that of the precipitate formed in the exchange reaction (K_{j}^{sp}) . For univalent ions from the solubility products of precipitates [47,131]:

$$K_{ij}^{pot} = \frac{K_{i}^{sp}}{K_{j}^{sp}}$$
(5.36)

5.3 Synopsis

In conclusion, in this chapter experimental techniques for measuring the activity of the electrolytes in aqueous solutions have been briefly reviewed. An overview of how Ion-Selective Electrodes (ISE) can be applied to carry out potentiometry and how to calculate the activity of a salt in solution by using both a reference electrode and an ISE as a reference electrode has been given. Finally, separate solution techniques to experimentally measure the selectivity coefficient of ISE's were reviewed. This survey of the available techniques and equations is necessary before selecting an appropriate experimental method. Having these informations permits the description of the experimental techniques in order to measure mean ionic activity coefficients of electrolytes in ternary systems.

Chapter 6

Measurement of the Mean Ionic Activity Coefficient of Electrolytes in Ternary Systems

6.1 Introduction

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In Chapter 5 potentiometric methods were reviewed and the application of ionselective electrodes to perform emf cell measurements was discussed. In this chapter, techniques for emf measurements and the calculation of the mean ionic activity coefficient of electrolytes in ternary systems will be briefly described. For completeness, Harned's rule, the application of the Gibbs-Duhem equation, and the Maxwell relation in terms of mean activity coefficients for ternary systems will be reviewed.

For a ternary system which consists of two non-volatile electrolytes and water, unless the measurements of the activity of the water are made in a well defined form, the data do not lead to the computation of the individual mean ionic activities of the electrolytes. An alternative is to measure the mean ionic activity of one of the salts. In fact, by keeping the total ionic strength of the mixture constant, as indicated by Pitzer [85] "one can obtain activity coefficient of all the components of a solution if the activity coefficient of a single component is obtained as a function of all concentrations." Therefore it is possible to calculate the activity coefficient of one of the electrolytes if one can measure the activity coefficient of the other without the measurement of activity of the water. In the following section we will discuss how one can carry out an electrochemical cell experiment to obtain a series of measurements in ternary systems keeping the total ionic strength of the solution constant and changing the ratio of the ionic strength of individual salts. Measurements of the activity of one salt keeping the total ionic strength of the ternary solution constant permits the simplification of the Gibbs-Duhem equation and then the evaluation of the mean activity coefficient of the second salt. However this method for the calculation of the mean activity coefficient of the second salt is limited to ternary systems which obey Harned's Rule [65]. As proposed by Pitzer [85], for the general case one can use cross-differentiation of the mean activity coefficient of the salts to develop a series of equations from which the mean activity coefficient of the second salt can be calculated. These approaches will be discussed in this chapter.

The use of ion-selective electrodes to measure mean ionic activity coefficients of electrolytes has been reported for some ternary systems of aqueous electrolyte solutions with common ions [11,83,128]. However to the best of our knowledge emf methods are rarely used for ternary systems without a common ion.

6.2 **Previous Ternary Measurements**

Experimental data for many binary aqueous electrolyte solutions measured with emf cells have been reported in the literature [22]. However due to limitations of the application of ion-selective electrodes to multicomponent mixtures, experimental measurements reported for ternary aqueous electrolyte solutions are not as many as those for binary systems. The most important measurements for mean ionic activity coefficients in ternary systems reported in the literature are briefly reviewed here.

Lanier [83] used a sodium ISE versus a silver-silver chloride electrode to measure the mean activity coefficient of NaCl in aqueous ternary solutions at 298.15 K and at ionic strengths from 1 to 6. He reported experimental data for the NaCl-NaNO₃-H₂O system and the other ternary aqueous solutions. Butler and Huston [25] reported the measurements of mean ionic activity coefficients in aqueous solutions of NaCl-CaCl₂ and NaCl-MgCl₂. They used a sodium amalgam electrode against a chloride (Ag/AgCl) electrode. The experimental results of the above investigations show that the Harned's Rule fits the activity coefficient of NaCl at various total ionic strengths. Usha et al. [128] reported mean ionic activity coefficients for both electrolytes for the ternary aqueous system of NaBr and CaBr₂ at 298.15 K and at total ionic strengths from 0.1 to 7.5. They used Na and Ca ISE's as indicator electrodes and Br ISE as a reference electrode. Also the selectivity coefficients in the HBr-CaBr₂-H₂O system at various temperatures have been measured by Roy et al. [117]. They only measured the activity coefficient of HBr using a Br electrode with a hydrogen electrode as a reference electrode. Activity coefficients of CaBr₂ were calculated and interpreted in terms of Pitzer's formalism.

Butler and Huston [23] used a potassium liquid ion-exchange electrode to measure the mean activity coefficient of KCl in the KCl-NaCl-H₂O system. They assumed that the Nernst equation with its theoretical slope was obeyed and that the potassium ISE did not respond at all to sodium ions.

Padova [95] used a potassium sensitive glass electrode to measure mean activity coefficients of KCl in the KCl-KNO₃-H₂O system at 298.15 K and at ionic strengths from 0.2 to 2.5. These results are in good agreement with the results obtained by the isopiestic method using the McKay-Perring transform [116]. As stated by Butler [22] "because of its importance both in physiological systems and in the chemistry of sea water, the CaCl₂-NaCl multicomponent electrolyte system has been studied by ISE's more than any other." Other ternary systems have been studied using the sodiumselective glass electrode against various reference electrodes and ISE's as reference electrodes[22]. For instance, in NaCl-NaF-H₂O ternary system a LaF₃ membrane (Floride ISE) electrode was used as a reference electrode, together with sodium glass ISE and sodium amalgam electrodes [23].

Although the majority of experimental data reported in the literature are for aqueous electrolyte mixtures, during the last few years emf methods have also been used for the measurements of the mean ionic activity coefficient in non-aqueous electrolyte systems. However, the application of ISE's to non-aqueous electrolyte solutions is not straight forward, because as explained in Chapter 5, ion-exchange liquid membranes are usually very sensitive to non-aqueous solvents and they may be dissolved. Kakabadse [74] wrote an excellent review of the effect of solvents on potentials of cells with ISE's. Glass and solid state ISE's are suitable for some non-aqueous electrolyte systems. Activity coefficients for NaCl in ethanol-water mixture and in Na-Formate-NaCl system were measured by Esteso et al. [42,43].

6.3 Experimental Measurements

This section deals with the design of experiments and apparatus for emf cell measurements. Elements of the experimental system are presented in detail and the calibration of the ion-selective electrodes used in the experiments is discussed. The choice of aqueous ternary systems which have been used in the experiments are justified and the experimental procedure is presented.

6.3.1 A General View of the Apparatus

The apparatus which was designed and constructed to carry out electromotive force (emf) cell measurements consists of the various elements. The main features are a thermostatic cell, ion-selective electrodes, reference electrodes, a thermostatic bath, a mv meter, adapters, a temperature probe, magnetic stirrers, etc.

Figure (6.1) shows a schematic diagram of the experimental system. The thermostatic cell consists of a vertical aluminum cylindrical vessel. The top hd has a circular hole to allow the insertion of an approximately 500 ml sample beaker. The beaker is sealed in position by a metal flange, cushioned by a rubber ring and held in place by three screws. The electrodes and the temperature probe arc inserted through a rubber stopper into the beaker. The solution is agitated by a magnetic stirrer. The temperature of the thermostatic cell is controlled by water from a thermostatic bath which circulates in the concentric chamber between the beaker and the aluminum cylinder. The temperature of water in the thermostatic bath is stabilized using an additional cooling bath. Consequently the temperature of the cooling bath

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Figure 6.1: Schematic view of the experimental apparatus

is controlled by a cooling coil immersed in the cooling bath. The temperature of sample solution is held at 298.2 \pm 0.1 K.

6.3.2 Principal Elements of the Apparatus

The experimental apparatus consists of the three following major features:

I. Ion-Selective Electrodes (ISE):

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Five Orion ion-selective electrodes were used. Three of them are anionic and the other two are cationic.

- Ross sodium glass ISE (model 84-11)
- Calcium ion-exchanged ISE (model 93-20)
- Bromide solid state ISE (model 94-35)
- Chloride solid state ISE (model 94-17B)
- Nitrate ion-exchange ISE (model 93-07)

In addition, for pH control of the solution a Ross pH electrode (model 81-01) was used.

II. Reference Electrodes (Ref):

In addition to the use of an ISE as a reference electrode one single junction and one double junction electrodes was used as follows.

- 1. Reservoir reference electrode (Orion model 90-04, single junction). The filling solution is 4M KCl (saturated with respect to silver ion).
- 2. Double junction electrode (Orion model 90-02). This is a silver-type Ag/AgCl reference electrode with an outer chamber which isolates the inner reference element and filling solution from the sample. The inner chamber filling solution is an Orion Cat.No 900002 and the outer chamber filling solution is a 0.04m (NH₄)₂SO₄.

III. mv Meter and Temperature Probe:

As explained in the Chapter 5, in order to use an ISE as a reference electrode we need a dual electrometer with a very high internal impedance to monitor the mv changes in emf measurements. An Orion PH/ISE meter model EA 920 was used. This model has a large, easy-to-read, custom LCD (Liquid Crystal Display). It has two inputs with BNC (Bayonet Neil-Concelman) connectors for the indicator ISE's and two inputs with pin-tip connectors for reference electrodes. Since we wanted to use an ISE as a reference electrode, a BNC-pin-tip adapter was connected to the reference ISE and inserted into the pin-tip reference input.

The temperature of the sample was controlled by an Orion Automatic Temperature Compensation (ATC) probe (model 917001). This probe transmits a signal to the mv meter, which automatically corrects pH and mv measurements for variation in the electrode slope due to temperature changes.

6.3.3 Salts, Water and Preparation of Solutions

The following reagent grade salts were used without further purification:

- Sodium B. Jmide, NaBr (Anachemia, AC-8272)
- Sodium Chloride, NaCl (Anachemia, AC-8304)
- Sodium Nitrate, NaNO₃ (A & C, 5337)
- Calcium Chloride, CaCl₂.2H₂O (Anachemia, AC-1946)
- Calcium Nitrate, $Ca(NO_3)_2.4H_2O$ (A & C, C1305)

A purification water unit was used to prepare very high quality de-ionized water. The following three types of de-ionization columns were used:

- 1. Two absorber columns (Cole-Parmer, model N-01506-15) to produce water free of most organic compounds, free of chlorine, etc.
- 2. Two universal cartridges (Cole-Parmer, model W-01506-25). These cartridges produce water equivalent to single-distilled water.

3. Two research cartridges (Cole-Parmer, model N-01506-35). These cartridges produce water equivalent to triple-distilled water, removing all ionized minerals down to a level of 4 ppb or less.

These six cartridges were connected in series. First, tap water was passed through the absorbers and then through the universal and the research cartridges. Finally water was passed through a distillation unit to get very high quality pure water.

The stock solution of binary aqueous solutions of the salts were prepared initially for the total ionic strengths of the experimental run. The solutions were prepared by weighing the salts and then dissolving them in the required amount of pure deionized distilled water.

6.4 Calibration of ISE's in Binary Solutions

Before using the ISE's in ternary systems they should be calibrated in the binary solutions and the slope of the electrode should be experimentally determined. Some researchers have assumed that the ISE's have Nernstian behavior and they have used the Nernstian slope in their calculations. Although this method saves time, it introduces unnecessary errors so in our calculations we have used the slopes which we determined by regression analysis of the experimental values of emf measurements in binary solutions. Moreover, the selectivity coefficient of ISE's should be determined if any of the other ions in the solution interfere with the electrode of interest. The separate solutions method discussed in Chapter 5 was used to determine the selectivity coefficients of the ISE's. Before the determination of the selectivity coefficient of each electrode, one needs to construct the calibration curve for each binary solution. Each ISE should be calibrated in the binary solution containing the particular ion of the ISE and in the binary solution containing the interfering ion. For example the selectivity coefficient of Ca with respect to Na ions, K_{Ca-Na} , can be determined by calibrating a calcium ion selective electrode in both an aqueous solution of $CaCl_2$ and in an aqueous solution of NaCl. The ISE's were calibrated in five different binary aqueous mixtures. We will only describe in detail the calibration of the sodium and the calcium ion selective electrodes in NaBr aqueous solution and the results for the other ISE's will then be presented.

The following cell was set up to calibrate the sodium, calcium and bromide electrodes.

Detector Electrode	Binary solution	Reference electrode
Na-ISE		Bromide-ISE
Ca-ISE	NaBr-H ₂ O	Single Junction Electrode (SJE)
Br-ISE		Double Junction Electrode (DJE)

Two hundred ml of nine molal NaBr solution were placed in the beaker. All the electrodes and the temperature probe were immersed in the solution. The electrodes were connected to the mv-meter. The solution was agitated with a magnetic stirrer for one hour. When the system stabilized, the following signals were measured.

a: $E_{S}(Na^{+})$:	Na-ISE	VS.	SJE
b: $E_S(Ca^{++})$:	Ca-ISE	VS.	SJE
c: $\mathbf{E}_{S}(\mathbf{Br})$:	Br-ISE	VS.	SJE
d: $E_D(Na^+)$:	Na-ISE	VS.	DJE
e: $E_D(Ca^{++})$:	Ca-ISE	VS.	DJE
f: $\mathbf{E}_D(\mathbf{Br}^-)$:	Br-ISE	VS.	DJE
o E(NaBr)	Na-ISE	vs	Br-ISE
h: $E(CaBr_2)$:	Ca-ISE	VS.	Br-ISE

After those measurements were completed, the solution was diluted by adding pure deionized water and stabilized again. The measurements were continued until the molality of solution reached an ionic strength of the order of 0.01. When a single junction reference electrode is used, the cell equations for ISE's corresponding to the above measurements are:

$$a: E_{S}(Na^{+}) = E'(Na^{+}) + S_{1} \ln a(Na^{+})$$
(6.1)

$$b: E_{S}(Ca^{++}) = E'(Ca^{++}) + \frac{S_{3}}{2} \ln[K_{Ca-Na}a^{2}(Na^{+})]$$
(6.2)

$$c: E_{S}(Br^{-}) = E'_{S}(Br^{-}) - S_{2} \ln a(Br^{-})$$
 (6.3)

Then, assuming $S_1 \simeq S_2 \simeq \frac{S_1 + S_2}{2}$, subtracting the above equations and expressing the activity of ions in terms of the activity coefficient of NaBr leads to

$$E_{S}(\text{NaBr}) = E'_{S}(\text{NaBr}) + (\frac{S_{1} + S_{2}}{2})\ln(m\gamma_{\pm})^{2}$$
 (6.4)

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$$E'_{S}(\mathrm{NaBr}) = E'_{S}(\mathrm{Na^{+}}) - E'_{S}(\mathrm{Br^{-}})$$

In the above equations S_1 and S_2 are the slopes of the Na-ISE and the Br-ISE against the single junction electrode, respectively, and m and γ_{\pm} are the molality and mean ionic activity coefficient of NaBr.

Alternatively if we write the cell equation when the bromide ISE is used as a reference electrode.

$$g: E(\text{NaBr}) = E'(\text{NaBr}) + S \ln (m\gamma \pm)^2$$
(6.5)

As can be seen from the comparison of equations (6.4) and (6.5), the same form of calibration equation for the sodium ISE is obtained when we use a single junction reference electrode or when we use a bromide ISE as a reference electrode. The terms E'(NaBr) and $E'_S(NaBr)$ correspond to the same cell constant. The terms S and $\frac{s_1+s_2}{2}$ are the slope of the sodium ISE when we use bromide electrode or single junction electrode as a reference electrode and should be the same. We can also write the same form of the calibration equation for the case when a double junction reference electrode is used. As an example Figure (6.2) shows the calibration of the Na-ISE when the bromide ISE and the single junction electrode were used as a reference electrodes. Within the experimental error, the results are equivalent. As discussed in Chapter 5, the calibrations using an ISE as a reference electrode are preferred because they eliminate the effect of liquid junction potentials. Similar results were obtained for the other ISE's and are not reported in detail here.



Figure 6.2: Electromotive force of Na-ISE towards Br-ISE and single junction electrode in aqueous solution of NaBr at 298.2 K.

Note that the diamond symbols are superimposed to the square symbols in each and every point.

In these cell measurements, the calcium ISE was used in order to calculate the effect of interference of sodium ions towards this electrode. The same cell equations as for the sodium case can now be written as:

$$h: E(CaBr_2) = E'(CaBr_2) + \frac{S_4}{2} \ln [K_{Ca-Na}a^2(NaBr)]$$
 (6.6)

where:

$$E'(\operatorname{CaBr}_2) = E'(\operatorname{Ca}^{++}) - E'(\operatorname{Br}^{-})$$

 $a(\mathrm{NaBr}) = (m\gamma_{\pm})^2$

The activity of the NaBr and of the other salts in the binary salt-water solutions were calculated by the use of the mean activity coefficients of the respective salts from the tabulations of Robinson and Stokes [116] and of Hamer and Wu [63].

A similar set up of cells was prepared for the other binary solutions of interest and calibration curves were obtained in the same manner. All of the calibration parameters were evaluated by linear regression analysis of the experimental points In Appendix A, the experimental emf measurement data for calibration of ISE's and the method of linear regression are given in detail. Figure (6.3) to Figure (6.7) show the calibration lines of the sodium ISE and calcium ISE towards chloride and nitrate ISE's. As one can see from Figures (6.2) to (6.4) the responses of sodium ISE in binary aqueous solutions of NaBr, NaCl and NaNO₃ are straight lines. The cell constants and slope of sodium and calcium ISE's in the various binaries are shown in Table (6.1).

The responses of calcium ISE in the binary solutions of $CaBr_2$, $Ca(NO_3)_2$ and $CaCl_2$ are not linear over the whole range of the concentration. For instance, the response of Ca-ISE is linear up to a $CaCl_2$ molality of unity and its slope is very close to a Nernstian slope. The worse case is the response of Ca-ISE in $Ca(NO_3)_2$ solution. As one can see from Figure (6.7) when the nitrate ISE is used as a reference electrode, the Ca-ISE response is linear only at very low concentrations of the



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Figure 6.3: Electromotive force of Na-ISE towards NO3-ISE in aqueous solution of NaNO3 at 298.2 K.



Figure 6.4: Electromotive force of Na-ISE towards CI-ISE in aqueous solution of NaCl at 298.2 K.



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Figure 6.5: Electromotive force of Ca-ISE towards Br-ISE in aqueous solution of $CaBr_2$ at 298.2 K.



Figure 6.6: Electromotive force of Ca-ISE towards NO3-ISE in aqueous solution of Ca(NO₃)₂ at 298.2 K.



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Figure 6.7: Electromotive force of Ca-ISE towards CI-ISE in aqueous solution of CaCl₂ at 298.2 K.

$E = E' + S \ln(a)$ $a = activity$						
Ion Selective Electrode (ISE)	Reference Electrode (ISE)	Binary Solution	Maxımum Molahıty	<i>E</i> ′ (mv)	Electrode Slope (S)	correlation coefficient x 100 %
Sodium (Na ⁺)	Bromide (Br ⁻)	NaBr	90	445 913	25 465	99 97
Sodium (Na ⁺)	Nitrate (NO_3^-)	NaNO3	80	307 884	24 519	99-82
Sodium (Na ⁺)	Chloride (Cl ⁻)	NaCl	60	291 122	25 207	99-99
Calcium (Ca ⁺⁺)	Bromide (Br ⁻)	CaBr ₂	0 10	152 930	9 770	99.58
Calcium (Ca ⁺⁺)	Nitrate (NO_3^-)	$Ca(NO_3)_2$	0 05	78 435	11-429	99-79
Calcium (Ca ⁺⁺)	Chloride (Cl ⁻)	CaCl ₂	10	69 661	12 570	99 998

Table 6.1: Slopes and electrochemical constants of the various ISE's in different binary aqueous solutions at 298.2 K.

primary ion, Ca^{++} . At higher concentrations, the response deviates from linearity and tends to level off. The response of the Ca-ISE and of the NO₃-ISE, when a single junction electrode is used as a reference electrode, are shown in Figures (6.8) and (6.9), respectively. In these cases the activity of ions were calculated by NRTL-NRF model as discussed in Chapter 4. As one can observe from Figure (6.8) the slope of the response of the Ca-ISE at very low concentrations of NO₃⁻ ions is positive. However, when the concentration of nitrate ions increases the slope decreases and at a very high concentration of nitrate ions the sign of the slope of Ca-ISE becomes negative. The response of the nitrate electrode in a Ca(NO₃)₂ solution is also linear and negative at low concentrations of Ca⁺⁺ ions. However at higher concentrations of the calcium ions the slope of the NO₃-ISE changes.

The change of sign of the slope of the Ca-ISE in different binary solutions, particularly in the $Ca(NO_3)_2$ solution, clearly shows the interference of counter ions such as NO_3^- with the electrode membrane. As explained in Chapter 5, the calcium ion selective electrode is a liquid-membrane electrode which is based on ion exchange



Figure 6.8: Electromotive force of Ca-ISE towards single junction electrode in aqueous solution of Ca(NO3)2 at 298.2 K.

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Figure 6.9: Calibration of NO3-ISE towards single junction electrode in aqueous solution of Ca(NO3)2 at T=298.2 K.

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of compounds and neutral carriers [35,44]. The phenomenon of anion interference has been discussed for potassium liquid membrane ISE's [35,44]. Several theories have been proposed in literature to explain this phenomenon [19]. However our objective here is not to enter into the discussions of these theories but to suggest that the anionic interference in the response of the Ca-ISE at high concentration of anions may have the same causes as in the case of the potassium liquid membrane ISE. As indicated by Covington [35] "the deterioration in response, at high concentrations of primary ion, observed for certain counterions may be explained by consideration of a possible mechanism of ion transport across the membrane." Covington [35] also added " for membranes made of large lipophilic anions, such as thiocyanate and picrate, anion entry certainly occurs, there by effectively lowering the transport number of the cation, causing a deterioration in response, often to the extent of slope reversal."

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In conclusion, to close up this section, we have found technological limitations to measuring the mean activity coefficients in mixtures of $Ca(NO_3)_2$, $CaBr_2$ and $CaCl_2$ with the other electrolytes. Thus the measurements of mean activity coefficients of $Ca(NO_3)_2$ in a ternary system of $Ca(NO_3)_2$ and NaBr is not practically accessible by emf measurements. We can only measure the activity of NaB1 using ISE's and then calculate the activity of $Ca(NO_3)_2$ by cross-differentiation of the mean activity coefficient. This method will be discussed in some detail at the end of this chapter.

6.5 Measurements for Ternary Systems

The experimental objective of this work is to measure the mean activity coefficient of the electrolytes in a ternary aqueous solution of two salts. Several ternary systems involving a common ion and some without a common ion were considered as potential candidates. At the beginning the aqueous solution of $CaBr_2$ and NaCl as a case without a common ion was chosen. The emf of the sodium ISE using chloride and bromide ISE's as reference electrodes was measured. However after a few measurements, it was observed that the membrane of the chloride electrode was damaged and finally the membrane dissolved in the solution. The reason for this, as we painfully learned after, is that the following precipitation reaction occurs.

$$Br^- + AgCl \rightleftharpoons AgBr + Cl^-$$

where equilibrium constant of the reaction is:

$$K = \frac{a(\mathrm{Cl}^{-})}{a(\mathrm{Br}^{-})}$$

As was discussed by Freiser [47], one can write:

$$K = \frac{K^{SP}(\text{AgCl})}{K^{SP}(\text{AgBr})} = \frac{10^{-9.75}}{10^{-12.31}} = 10^{2.56}$$

As explained in Chapter 5, the selectivity coefficient of a solid state electrode is equal to the equilibrium constant of the precipitating ions reaction. Thus the selectivity coefficient of Cl-ISE towards Br-ISE is $10^{2.56}$. In other words, although it sounds absurd we can conclude that the chloride ISE is much more selective to bromide ions than to the chloride ions for which is advertised. Therefore in using an Cl-ISE to measure the activity of $a(Cl^{-})$, bromide ions must be absent or at concentrations less than $10^{-2.56}$ times the lowest $a(Cl^{-})$ level anticipated [47]. For this reason, ternary systems containing both bromide and chloride ions were eliminated from our list of experiments. Therefore, for our study we chose the following ternary systems:

- 1. NaCl NaNO₃ H_2O (a system with a common ion)
- 2. NaBr NaNO₃ H_2O (a system with a common ion)
- 3. NaBr $Ca(NO_3)_2$ H_2O (a system with no-common ion)

The first system, previously measured by Lanier [83], was selected so as to be able to standardize the experimental procedure and to verify the reproducibility of the data. The second system was measured because it provides a useful complement to the previous one and to the best of our knowledge no experimental data for the mean activity coefficient have been reported for it. The third system does not involve any common ion and was selected so to as study the mean activity coefficient of NaBr at high concentrations of $Ca(NO_3)_2$. One of our objectives was to provide new data for an electrolyte in an aqueous mixture without a common ion. This system represents the best compromise using available ion selective electrodes which do not present interference.

6.5.1 Experimental Procedure for Ternary Systems

For each of the above ternary systems, an emf cell was arranged. For instance for the aqueous solution of NaBr and $Ca(NO_3)_2$ the following cell was set up:

Detector Electrode	Ternary Solution	Reference Electrode
	$NaBr(I_1)$	Bromide-ISE
Na-ISE	$Ca(NO_3)_2$ (I ₂)	Single Junction Electrode (SJE)
		Double Junction Electrode (DJE)

The potential of a Na-ISE towards a Br-ISE, the single junction and the double junction electrodes were measured at different values of the molalities of the salts with constant total ionic strength $(I = I_1 + I_2)$ of the solution. In calculations of the mean ionic activity coefficients the measurements were obtained using the Br-ISE as a reference electrode. However the potentials were measured with respect to the SJE and the DJE in order to check the accuracy of the measurements. As an example, in Appendix C the data are shown for the system NaBr-Ca(NO₃)₂-H₂O but were not used in the calculations.

The experimental procedure was as follows. A two hundred ml binary solution of NaBr of total ionic strength I was placed in the beaker. The sodium and the bromide ISE's and the single and double junction reference electrodes were immersed in the solution. The temperature probe and the pH electrode were also placed in the mixture to check the temperature and the variation of the pH of the solution. All the electrodes were allowed to stay in binary NaBr mixture for one hour so that the stability of the potentials to within ± 0.1 mv could be ascertained. The following measurements were monitored for binary solutions of NaBr at a given ionic strength I.

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E°(NaBr) :	Na-ISE	VS.	Bromide-ISE
$E_S^o(Na)$:	Na-ISE	VS.	Single Junction Electrode
$E_D^o(Na)$:	Na-ISE	VS.	Double Junction Electrode
$\mathbf{E}^{o}_{S}(\mathbf{Br}):$	Br-ISE	VS.	Single Junction Electrode
$\mathbf{E}^{o}_{D}(\mathbf{Br})$:	Br-ISE	VS.	Double Junction Electrode

After measurements in the binary NaBr solution, $Ca(NO_3)_2$ solution of a similar ionic strength I was added. In principle, when two binary aqueous solutions of the same jonic strength are mixed, the total jonic strength of the ternary mixture will be the same as the ionic strength of the binaries. The way to calculate the ionic strength of individual salts in the mixture is shown in Appendix E. A titration technique was used to alter the composition of the mixture. This method allows one to minimize errors arising from sudden shifts in potential which are unrelated to changes in solution composition. Thus the cell was not disturbed during a series of measurements and the electrodes were always in place during the measurements. Due to the limitations in the volume of the beaker, two sets of potential measurements were made. In the first set, the experimental measurements were carried out starting with NaBr solution and using $Ca(NO_3)_2$ as titrant and in the second set the order was reversed. In the central region of composition the two runs overlap. This is used as a test for reproducibility of the data. The two half curves must overlap smoothly, otherwise either there is an error in emf measurements or the electrodes are not reversible. After adding a certain volume of titrant and allowing the solution to reach equilibrium (15min-30min) the following potentials were monitored.

E (NaBr) :	Na-ISE	VS.	Bromide-ISE
E_S (Na):	Na-ISE	VS.	Single Junction Electrode
E_D (Na):	Na-ISE	VS.	Double Junction Electrode
\mathbf{E}_{S} (Br):	Br-ISE	VS.	Single Junction Electrode
E_D (Br):	Br-ISE	VS.	Double Junction Electrode

As explained before, measurements with calcium and nitrate ISE's were not possible due to the interference of nitrate ions with the calcium electrode. The same technique for potential measurements has been carried out for aqueous solutions of NaBr-NaNO₃ and NaCl-NaNO₃. The details of the formulation of equations and the reduction of data in order to calculate the mean ionic activity coefficients of NaBr in NaBr-NaNO₃-

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 H_2O and NaBr-Ca(NO₃)₂- H_2O systems are discussed in Chapter 7.

6.6 Harned's Rule

Harned's rule is a linear model which have been widely used for the interpretation of changes of mean ionic activity coefficients of electrolytes in ternary aqueous solutions. For a ternary mixture of water, electrolyte 1 and electrolyte 2 with a constant total ionic strength I and a varying ionic strength of salt "2", *i.e.*, I_2 , it was empirically found that, in many cases, the logarithm of the mean activity coefficient of salt 1, $\ln \gamma_{\pm 1}$, varied linearly with I_2 or with $Y_2 = I_2/I$ [65,85,116], then

$$\ln \gamma_{\pm 1} = \ln \gamma_{\pm 1}^{\circ} - \alpha_{12}^{\prime} I_2 \tag{6.7}$$

where γ_{\pm}^{o} is the mean ionic activity coefficient of a pure electrolyte 1 in an aqueous solution at the same total ionic strength of the mixture, *i.e.*, *I*. The coefficient α'_{12} is an empirical coefficient which is called Harned's coefficient of salt 1 and it may be a function of the total ionic strength *I*. The original Harned's Rule used base ten logarithm, *i.e.*, $\alpha'_{12} = (\ln 10)\alpha_{12}$, where α_{12} is the reported Harned's coefficient in literature. The corresponding equation for the electrolyte 2 is

$$\ln \gamma_{\pm 2} = \ln \gamma_{\pm 2}^{o} - \alpha_{21}^{\prime} I_{1}$$
(6.8)

where $\gamma_{\pm 2}^{\circ}$ is the mean activity coefficient of pure salt 2 in the aqueous solution of ionic strength *I*. Equations (6.7) and (6.8) can also be written in terms of the ionic strength fraction of salt 2 and 1, *i.e.*, Y₂ and Y₁, respectively.

Trace activity coefficients are very important in electrolyte solutions because they facilitate a more detailed comparison of the effect of one electrolyte on the other in the mixture. The trace activity coefficient of electrolyte 1 in a ternary mixture is the value of activity coefficient of salt 1 in the presence of salt 2 extrapolated to zero concentration of salt 1 at constant ionic strength I. Thus, by using equations (6.7) and (6.8), the trace activity coefficient of salt 1 and 2 may be written as

$$\ln \gamma_{\pm 1}^{tr} = \ln \gamma_{\pm 1}^{o} - \alpha_{12}^{\prime} I \tag{6.9}$$

$$\ln \gamma_{\pm 2}^{tr} = \ln \gamma_{\pm 2}^{o} - \alpha_{21}^{\prime} I \tag{6.10}$$

where $I = I_1 + I_2$, is the total ionic strength of the mixture. By substituting eq. (6.9) in (6.7) we can obtain another useful equation as

$$\ln \gamma_{\pm 1} = \ln \gamma_{\pm 1}^{tr} + \alpha_{12}^{\prime} I_1 \tag{6.11}$$

similarly,

$$\ln \gamma_{\pm 2} = \ln \gamma_{\pm 2}^{tr} + \alpha_{21}^{\prime} I_2 \tag{6.12}$$

Equations (6.11) and (6.12) are useful for the calculation of mean ionic activity coefficients of salts in terms of their own ionic strength. This makes it possible to compare these values with those of the mean activity coefficient of the electrolyte in a binary aqueous mixture at the same ionic strength of the ternary system. Clearly when either I_1 or I_2 tends to zero, in a ternary mixture, the activity coefficient of trace electrolytes 1 or 2 will be obtained, respectively

Harned's Rule has proved to be valid for many ternary electrolyte systems at low concentrations. However, for some systems, departure from linearity in the mean activity coefficients as a function of the total ionic strength occurs and it has been necessary to add more terms with empirical coefficients. Thus, the general expressions are [85].

$$\ln \gamma_{\pm 1} = \ln \gamma_{\pm 1}^{o} - \alpha_{12}^{\prime} I_2 - \beta_{12}^{\prime} I_2^2 \dots$$
(6.13)

$$\ln \gamma_{\pm 2} = \ln \gamma_{\pm 2}^{o} - \alpha_{21}^{\prime} I_1 - \beta_{21}^{\prime} I_1^2 \dots$$
(6.14)

Equations similar to eqs (6.11) and (6.12) can not be obtained when the nonlinear equations (6.13) and (6.14) are used. As stated above, Harned's Rule is a very useful model for many ternary aqueous electrolyte systems. In the next section we will review the method to compute the mean activity coefficient of the second salt when the mean activity coefficient of the first salt can be obtained experimentally. This method assumes that both salts follow Harned's Rule.

6.7 The Gibbs–Duhem Equation for Ternary Systems

For completeness, we review here the use of the Gibbs-Duhem equation for ternary systems. The Gibbs Duhem equation for a single liquid phase ternary system at constant temperature and neglecting the small effect due to equilibrium pressure changes can be written as:

$$n_1 d\mu_1 + n_2 d\mu_2 + n_W d\mu_W = 0 \tag{6.15}$$

where n_1 and n_2 are the number of moles of salts and n_W is the number of moles of water. The corresponding chemical potentials are μ_1 , μ_2 , μ_W . As was described in Chapter 2, the chemical potentials of the salts and water can be written in terms of the activity and the number of moles can be expressed in terms of ionic strength. Thus for an electrolyte, one can write:

$$I_{i} = \frac{1}{2} (\nu_{i}^{+} Z_{+i}^{2} + \nu_{i}^{-} Z_{-i}^{2}) m_{i} = K_{i} m_{i}$$
(6.16)

where

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$$K_{i} = \frac{1}{2} \left(\nu_{i}^{+} Z_{+i}^{2} + \nu_{i}^{-} Z_{-i}^{2} \right)$$
(6.17)

Therefore, for an aqueous mixture equation (6.15) can be written as:

$$\frac{I_1}{K_1} d \ln a_1 + \frac{I_2}{K_2} d \ln a_2 = -55.51 d \ln a_W$$
(6.18)

As discussed in Chapter 2, the activity of the salt can be written as

$$a_i = \nu_{\pm i} m_i^{\nu_i} \gamma_{\pm i}^{\nu_i}$$

thus

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$$d \ln a_{i} = \nu_{i} d \ln(m_{i} \gamma_{\pm i}) = \nu_{i} d \ln(\frac{I_{i}}{K_{i}} \gamma_{\pm i})$$
(6.19)

Writing eq. (6.19) for both salts, assuming validity of eqs (6.7) and (6.8), and substituting into eq. (6.18) yields:

$$\left(\frac{\nu_1}{K_1}\alpha'_{12} + \frac{\nu_2}{K_2}\alpha'_{21}\right)Y_1 dY_1 - \frac{\nu_2}{K_2}\alpha'_{21}dY_1 + \left(\frac{\nu_1}{K_1} - \frac{\nu_2}{K_2}\right)\frac{dY_1}{I} = -\frac{55.51}{I^2}d\ln a_W$$
(6.20)

where $Y_1 = I_1/I$ and $I_2 = (1 - Y_1)I$ with $I = I_1 + I_2$ constant. Equation (6.20) is then integrated at constant I and T from $Y_1=0$ (pure salt ?) to $Y_1=1$ (pure salt 1) to give:

$$\frac{1}{2}\left(\frac{\nu_{1}}{K_{1}}\alpha_{12}'+\frac{\nu_{2}}{K_{2}}\alpha_{21}'\right)-\frac{\nu_{2}}{K_{2}}\alpha_{21}'$$

$$+\frac{1}{I}\left(\frac{\nu_{1}}{K_{1}}-\frac{\nu_{2}}{K_{2}}\right) = -\frac{55.51}{I^{2}}\ln\frac{a_{W}^{\circ}(1)}{a_{W}^{\circ}(2)}$$
(6.21)

As discussed in Chapter 2, the activity of water can be written in terms of its osmotic coefficient. At a total ionic strength I

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$$\ln a_W^o = -\frac{\nu_i m_i}{55.51} \phi_i^o = -\frac{\nu_i I}{55.51 K_i} \phi_i^o$$
(6.22)

with:

$$\phi_i^o = 1 + \frac{1}{I} \int_0^I d \ln \gamma_{\pm,}^o$$
(6.23)

Thus combining eqs (6.21) to (6.23),

$$\frac{\nu_1}{K_1} \alpha'_{12} - \frac{\nu_2}{K_2} \alpha'_{21} = \frac{2}{I^2} \int_0^I Id \ln\left[\frac{(\gamma_{\pm 1}^o)^{\nu_1/K_1}}{(\gamma_{\pm 2}^o)^{\nu_2/K_2}}\right]$$
$$= \frac{2}{I} \left[\frac{\nu_1}{K_1} (\phi_1^o - 1) - \frac{\nu_2}{K_2} (\phi_2^o - 1)\right]$$
(6.24)

Therefore, if either α'_{12} or α'_{21} is known by experiment, the other may be calculated from the osmotic coefficients or the mean activity coefficients of the binary solutions by the use of equation (6.24).

In the case of a ternary system with uni-univalent electrolytes, equation (6.24) can be written as:

$$\alpha'_{21} - \alpha'_{12} = \frac{2}{I^2} \int_0^I I \, d \, \ln[\frac{\gamma^o_{\pm 2}}{\gamma^o_{\pm 1}}] = \frac{2}{I} (\phi^o_2 - \phi^o_1) \tag{6.25}$$

Similarly, assuming that Harned's Rule is valid, the equations for the ternary system of NaBr(1) and $Ca(NO_3)_2(2)$ can be written as:

$$\alpha_{21}' - 2\alpha_{12}' = \frac{2}{I^2} \int_0^I I \, d \, \ln[\frac{\gamma_{\pm 2}^\circ}{(\gamma_{\pm 1}^\circ)^2}] = \frac{2}{I} (1 + \phi_2^\circ - 2\phi_1^\circ) \tag{6.26}$$

6.8 Maxwell Relations for Activity Coefficients

For completeness, we review here some consequences of the Maxwell relation. Since chemical potentials have exact differentials, one can write at constant T and P,

$$\left(\frac{\partial\mu_1}{\partial n_2}\right)_{n_1} = \left(\frac{\partial\mu_2}{\partial n_1}\right)_{n_2} \tag{6.27}$$

using eq. (2.28)

$$\nu_1 \left(\frac{\partial \ln \gamma_{\pm 1}}{\partial m_2}\right)_{m1} = \nu_2 \left(\frac{\partial \ln \gamma_{\pm 2}}{\partial m_1}\right)_{m2} \tag{6.28}$$

Equation (6.28) is the Maxwell relation or cross-differentiation equation for the mean activity coefficients in a ternary system. Using eqs (6.13) and (6.14) the equations for the mean activity coefficients can be written as

$$\ln \gamma_{\pm 1} = \ln \gamma_{\pm 1}^{\circ} - \alpha_{12}' I_2 - \beta_{12}' I_2^2$$
(6.29)

$$\ln \gamma_{\pm 2} = \ln \gamma_{\pm 2}^{\circ} - \alpha_{21}' I_1 - \beta_{21}' I_1^2$$
(6.30)

where I_1 and I_2 are given by eq. (6.16). Thus using eq. (6.16), eq. (6.28) takes the form:

$$K_2 \nu_1 \left(\frac{\partial \ln \gamma_{\pm 1}}{\partial I_2}\right)_{I_1} = K_1 \nu_2 \left(\frac{\partial \ln \gamma_{\lambda,2}}{\partial I_1}\right)_{I_2}$$
(6.31)

Following Harned and Robinson [64], using eq. (6.29) and (6.30), it follows from eq. (6.31) that

$$K_{2}\nu_{1}\left[\left(\frac{\partial ln\gamma_{\pm 1}^{o}}{\partial I_{2}}\right)_{I_{1}} - \alpha_{12}^{\prime} - I_{2}\left(\frac{\partial \alpha_{12}^{\prime}}{\partial I_{2}}\right)_{I_{1}} - 2\beta_{12}^{\prime}I_{2} - I_{2}^{2}\left(\frac{\partial \beta_{12}^{\prime}}{\partial I_{2}}\right)_{I_{1}}\right] =$$

$$K_{1}\nu_{2}\left[\left(\frac{\partial ln\gamma_{\pm 2}^{o}}{\partial I_{1}}\right)_{I_{2}} - \alpha_{21}^{\prime} - I_{1}\left(\frac{\partial \alpha_{21}^{\prime}}{\partial I_{1}}\right)_{I_{2}} - 2\beta_{21}^{\prime}I_{1} - I_{1}^{2}\left(\frac{\partial \beta_{21}^{\prime}}{\partial I_{1}}\right)_{I_{2}}\right]$$
(6.32)

Following Pitzer [85], since $I=I_1+I_2=$ constant, the partial derivative of any function g can be transformed to the total derivative as follows:

$$(\frac{\partial g}{\partial I_2})_{I_1} = (\frac{\partial g}{\partial I})_{I_1} = \frac{dg}{dI}$$

Using $I_1=Y_1I$ and $I_2=(1-Y_1)I$, one can simplify eq. (6.32) and since the resultant equation holds for all values of Y_1 , then if we write the equation in a form of polynomial of the variable Y_1 , the coefficients should be zero, *i.e.*,

$$-\frac{d}{dI}\left[ln\frac{(\gamma_{\pm 2}^{o})^{K_{1}\nu_{2}}}{(\gamma_{\pm 1}^{o})^{K_{2}\nu_{1}}}\right] + K_{1}\nu_{2}\alpha_{21}' - K_{2}\nu_{1}\alpha_{12}' - K_{2}\nu_{1}I\frac{d\alpha_{12}'}{dI}$$
$$-2K_{2}\nu_{1}I\beta_{12}' - K_{2}\nu_{1}I^{2}\frac{d\beta_{12}'}{dI} = 0 \qquad (6.33)$$

$$\frac{d}{dI}(K_1\nu_2\alpha'_{21} + K_2\nu_1\alpha'_{12}) + 2(K_1\nu_2\beta'_{21} + K_2\nu_1\beta'_{12}) + 2K_2\nu_1I\frac{d\beta'_{12}}{dI} = 0$$
(6.34)

$$\frac{d}{dI}(K_1\nu_2\beta'_{21} - K_2\nu_1\beta'_{12}) = 0$$
(6.35)

From these general equations, several particular situations may arise; we consider here two important cases:

Case a:

The case in which both salts follow Harned's Rule. In this case, both β'_{12} and β'_{21} are zero and eq. (6.34) can be integrated to give

$$K_1 \nu_2 \alpha'_{21} + K_2 \nu_1 \alpha'_{12} = \text{constant}$$
(6.36)

For uni-univalent electrolyte mixtures, eq. (6.36) takes the form (at constant temperature):

$$\alpha'_{21} + \alpha'_{12} = \text{constant} \tag{6.37}$$

If, in a ternary system, both salts follow Harned's Rule and in addition the Harned's coefficients are independent of total ionic strength, eq. (6.33) takes the following form for uni-univalent electrolyte mixtures:

$$\alpha'_{21} = \alpha'_{12} + \frac{d}{dI} \left(\ln \frac{\gamma^{*}_{\pm 2}}{\gamma^{*}_{\pm 1}} \right)$$
(6.38)

Combining eqs (6.25) and (6.38), one obtains:

$$\frac{d}{dI}(\ln\frac{\gamma_{\pm 2}^{\circ}}{\gamma_{\pm 1}^{\circ}}) = \frac{2}{I^2} \int_0^I I \, d(\ln\frac{\gamma_{\pm 2}^{\circ}}{\gamma_{\pm 1}^{\circ}}) \tag{6.39}$$

Equation (6.39) is only valid when $\ln \frac{\gamma_{\pm 2}^{*}}{\gamma_{\pm 1}^{*}}$ is linear with respect to the total ionic strength.

Case b:

If salt 1 follows Harned's Rule, *i.e.*, $\beta'_{12} = 0$, and salt 2 follows eq. (6.30), then eqs (6.34) and (6.35) can be integrated to give

$$K_1 \nu_2 \alpha'_{21} + K_2 \nu_1 \alpha'_{12} + 2I K_1 \nu_2 \beta'_{21} = \text{constant}$$
(6.40)

with

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$$\beta'_{21} \simeq \text{constant} \quad (T = \text{constant})$$

Following Harned and Robinson [64], eq. (6.32) can be written as

$$K_{1}\nu_{2}\left(\frac{\partial I_{1}(\alpha'_{21} + \beta'_{21}I_{1})}{\partial I}\right)_{I_{2}}$$
$$= \frac{d}{dI}\left[\ln\frac{(\gamma^{*}_{\pm 2})^{\nu_{2}K_{1}}}{(\gamma^{*}_{\pm 1})^{\nu_{1}K_{2}}}\right] + K_{2}\nu_{1}I_{2}\frac{\partial \alpha'_{12}}{\partial I} + K_{2}\nu_{1}\alpha'_{12} \quad (6.41)$$

with I_2 constant. Integration of eq. (6.41) between the lower limit of $I=I_2$, $I_1=0$ and $I=I_1+I_2$ gives

$$K_1 \nu_2 I_1(\alpha'_{21} + \beta'_{21} I_1) = \ln \frac{(\gamma^{\circ}_{\pm 2})^{\nu_2 K_1}}{(\gamma^{\circ}_{\pm 1})^{\nu_1 K_2}} + K_2 \nu_1 I_2[\alpha'_{12}]_{I_2}^I + K_2 \nu_1 \int_{I_2}^I \alpha'_{12} dI \quad (6.42)$$

Two special cases can be considered, as I_1 approaches I and I_2 approaches zero, eq. (6.42) becomes

$$K_1 \nu_2 I(\alpha'_{21} + \beta'_{21}I) = \ln \frac{(\gamma^o_{\pm 2})^{\nu_2 K_1}}{(\gamma^o_{\pm 1})^{\nu_1 K_2}} + K_2 \nu_1 \int_0^I \alpha'_{12} dI$$
(6.43)

Also when I_2 approaches I and I_1 approaches zero, it is convenient to rewrite eq. (6.41) as

$$K_{1}\nu_{2}(\alpha'_{21} + \beta'_{21}I_{1}) + K_{1}\nu_{2}I_{1}(\frac{\partial(\alpha'_{21} + \beta'_{21}I_{1})}{\partial I})_{I_{2}}$$

$$= \frac{d}{dI}\left[\ln\frac{(\gamma^{o}_{\pm 2})^{\nu_{2}K_{1}}}{(\gamma^{o}_{\pm 1})^{\nu_{1}K_{2}}}\right] + K_{2}\nu_{1}I_{2}\frac{\partial\alpha'_{12}}{\partial I} + K_{2}\nu_{1}\alpha'_{12}$$
(6.44)

and in the limit as I_1 approaches zero

$$K_1 \nu_2 \alpha'_{21} = \frac{d}{dI} \left[\ln \frac{(\gamma_{\pm 2}^o)^{\nu_2 K_1}}{(\gamma_{\pm 1}^o)^{\nu_1 K_2}} \right] + K_2 \nu_1 I \frac{\partial \alpha'_{12}}{\partial I} + K_2 \nu_1 \alpha'_{12}$$
(6.45)

From eq. (6.42) one can obtain a linear function for $(\alpha'_{21} + \beta'_{21}I_1)$ so that the limits of this function at $I_1 = 0$ and $I_1 = I$ can be evaluated by eqs (6.45) and (6.43), respectively. Thus, the intercept of this line gives α'_{21} and β'_{21} can be calculated from the slope of this line.

Thus if one salt obeys Harned's Rule the other salt will obey Harned's Rule provided that eq (6.37) is satisfied. Similarly if one electrolyte follows Harned's Rule and the other electrolyte follows eq. (6.30), relation (6.40) should hold. In the next chapter the application of equations (6.38) or (6.25) to the ternary system NaBr-NaNO₃-H₂O will be shown. Also eqs (6.43) and (6.45) will be used for the ternary system NaBr-Ca(NO₃)₂-H₂O.

6.9 Synopsis

In conclusion, in this chapter the application of emf cells to ternary aqueous electrolyte systems was discussed. The experimental apparatus and also the calibrations of ISE's were described in detail. The ternary systems to be measured were selected and the experimental procedure for ternary systems was discussed. Finally Harned's Rule and the application of the Gibbs-Duhem equation and Maxwell relations for ternary aqueous electrolyte systems were discussed. In the next chapter the experimental data will be presented and the mean activity coefficient of the second salt will be evaluated from the data of the first one.
Chapter 7

Reduction of Data and Experimental Results for Ternary Aqueous Electrolyte Systems

7.1 Introduction

In this chapter the reduction of emf measurements data for the three ternary systems $NaCl-NaNO_3-H_2O$, $NaBr-NaNO_3-H_2O$ and $NaBr-Ca(NO_3)-H_2O$ will be discussed. Also the calculation of the mean ionic activity coefficient of the second salt, *i.e.*, $NaNO_3$ and $Ca(NO_3)_2$ using the Gibbs-Duhem equation and Maxwell relations will be presented. The presentation is initiated by discussing the determination of the selectivity coefficients of the sodium, calcium and nitrate ISE's.

7.2 Selectivity Coefficients of the ISE's

The separate solution method was used to evaluate the selectivity coefficients of all the Ion-Selective Electrodes. Repeated experimental measurements under different conditions showed that the bromide ISE is completely selective to bromide ions and

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does not have any interference with nitrate ions. Thus one can assume a zero value for K_{Br-NO3} . The selectivity coefficient of the nitrate electrode by the calibration of the nitrate ISE in two different solutions of NaBr and NaNO₃ was evaluated. The calibration data are shown in Appendix D. A sodium ion selective electrode was used as an indicator electrode and a nitrate electrode as a reference electrode. As discussed in Chapter 5, one can write

$$E(\text{NaNO}_3)_{\text{NaNO}_3} = E'(\text{NaNO}_3) + S \ln a(\text{NaNO}_3)$$
(7.1)

$$E(\text{NaNO}_3)_{\text{NaBr}} = E'(\text{NaNO}_3) + S \ln [K_{NO_3 - Br}a(\text{NaBr})]$$
(7.2)

By subtracting eq. (7.1) from eq. (7.2) and using the equal activity method, one can obtain

$$K_{\text{NO}_3-\text{Br}} = exp[\frac{E(\text{NaNO}_3)_{\text{NaBr}} - E(\text{NaNO}_3)_{\text{NaNO}_3}}{S}]$$
(7.3)

where S is the slope of the Na-ISE when a NO₃-ISE is used as a reference electrode. The average value of $K_{NO_3-B_r}$ at low range concentrations of the bromide ions $(m \leq 0.3)$ in the solution was calculated as 0.135. A value of 0.13 for the Orion liquid ion exchanger in PVC/tetraoctyl/ammonium nitrate was reported by Pungor et al. [111]. Even when the term $K_{NO_3-B_r}$ is not used in the calculations, because the measurements by the NO₃-ISE were not reproducible for the ternary aqueous solutions, this agreement with a previously reported value of $\kappa'_{NO_3-B_r}$ is worth noticing

Similarly, the selectivity coefficient of the Na-ISE was evaluated by the separate solution method. We measured the response of the Na-ISE towards a NO₃-ISE in two separate binary solutions of Ca(NO₃)₂ and NaNO₃. Using the equal activity method, K_{Na-Ca} can be written as

$$K_{\text{Na-Ca}} = a^{\frac{1}{2}} (\text{NaNO}_3) exp[\frac{E(\text{NaNO}_3)_{\text{Ca}(\text{NO}_3)_2} - E(\text{NaNO}_3)_{\text{NaNO}_3}}{S}]$$
(7.4)

An average value of 0.707 x 10^{-3} was obtained at low concentrations of Na and Ca ions. At higher concentrations of Ca ions the value of K_{Na-Ca} decreased indicating that the Na-ISE is very selective to sodium ions. In fact the Orion manufacturer [37] claims that the Ross Na-ISE does not interfere with calcium ions in solution. Conversely, the selectivity coefficient of the Ca-ISE towards sodium ions was evaluated. The response of the Ca-ISE against a NO₃-ISE as a reference electrode was monitored in two separate binary solutions of NaNO₃ and Ca(NO₃)₂. The equal activity method was used so that the following equation can readily obtained,

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$$K_{\text{Ca-Na}} = \frac{1}{a(\text{NaNO}_3)} exp[\frac{E[\text{Ca}(\text{NO}_3)_2]_{\text{NaNO}_3} - E[\text{Ca}(\text{NO}_3)_2]_{\text{Ca}(\text{NO}_3)_2}}{S/2}] \quad (7.5)$$

An average value of 9.303 x 10^{-3} was obtained at low concentrations (m ≤ 0.05). All emf data related to selectivity coefficient measurements are reported in Appendix D.

7.3 The Mean Activity Coefficient of NaCl in Aqueous Solutions of NaCl and NaNO₃

The mean ionic activity coefficient of NaCl in ternary aqueous solution of NaCl and NaNO₃ was reported by Lanier [83]. The measurements for this system were repeated in order to verify the reproducibility of the present measurements and standardize the experimental procedure. As explained in the previous chapter, the following cell was set up.

Detector Electrode	Ternary Solution	Reference Electrode
	$NaCl(I_1)$	Chloride-ISE
Na-ISE	$NaNO_3$ (I ₂)	Single Junction Electrode
	i	Double Junction Electrode

The experiments were carried out starting with both pure NaCl(I) and NaNO₃(I) solutions at the same total ionic strength of the mixture $(I=I_1+I_2)$. For the binary solution of NaCl using the Cl-ISE as a reference electrode, Nikolsky-Eisenman equation can be written as

$$E^{\circ}(\text{NaCl}) = E'(\text{NaCl}) + S \ln a^{\circ}(\text{NaCl})$$
(7.6)

where a° (NaCl) is the activity of the NaCl in the binary NaCl-H₂O system for a given ionic strength I

$$a^{\circ}(\text{NaCl}) = [m^{\circ}(\text{NaCl})\gamma^{\circ}_{\pm}(\text{NaCl})]^{2}$$
(7.7)

where $m^{\circ}(NaCl)=I$ and $\gamma^{\circ}_{\pm}(NaCl)$ is the mean activity coefficient of NaCl in the binary solution at the total ionic strength *I*. Similarly, the Nikolsky-Eisenman equation can be written for the ternary system as:

$$E(\text{NaCl}) = E'(\text{NaCl}) + S \ln a(\text{NaCl})$$
(7.8)

Following Lanier, the selectivity coefficient of Cl-ISE towards nitrate ions was assumed to be negligible. Subtracting eqs (7.8) from (7.6), one readily obtains

$$E(\text{NaCl}) - E^{o}(\text{NaCl}) = S \ln \frac{a(\text{NaCl})}{a^{o}(\text{NaCl})}$$
(7.9)

where:

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$$a(\text{NaCl}) = m_1(m_1 + m_2)\gamma_{\pm}^2(\text{NaCl})$$
 (7.10)

 $m_1 = I_1 = I(\text{NaCl})$

 $m_2 = I_2 = I_2(\text{NaNO}_3)$

Substituting eqs (7.7) and (7.10) in eq. (7.9) yields:

$$\gamma_{\pm}^{2}(\text{NaCl}) = \frac{\left[\frac{m^{\circ}(\text{NaCl})\gamma_{\pm}^{\circ}\right]^{2}}{m_{1}(m_{1}+m_{2})}exp\left[\frac{E(\text{NaCl})-E^{\circ}(\text{NaCl})}{S}\right]$$
(7.11)

Substituting $m_1 + m_2 = m^o(\text{NaCl}) = I$ in eq. (7.11), and simplifying it gives

$$\gamma_{\pm}(\text{NaCl}) = \sqrt{\frac{I}{I(\text{NaCl})}} \gamma_{\pm}^{\circ}(\text{NaCl}) exp[\frac{E(\text{NaCl}) - E^{\circ}(\text{NaCl})}{2S}]$$
(7.12)

or

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$$\ln \gamma_{\pm}(\text{NaCl}) = \ln \gamma_{\pm}^{\circ}(\text{NaCl}) + \ln \sqrt{\frac{I}{I(\text{NaCl})}} + \frac{E(\text{NaCl}) - E^{\circ}(\text{NaCl})}{2S}$$
(7.13)

Following Lanier, eq. (7.13) is transformed to base ten logarithm as

$$\log \gamma_{\pm}(\text{NaCl}) = \log \gamma_{\pm}^{o}(\text{NaCl}) + \log \sqrt{\frac{I}{I(\text{NaCl})}} +$$

 $\frac{E(\text{NaCl}) - E^{\circ}(\text{NaCl})}{2(2.303)S}$ (7.14)

Equation (7.14) was used to calculate the mean activity coefficient of NaCl in the mixture. A linear regression analysis was used to fit the experimental data obtained by eq. (7.14). Experiments were performed for three different total ionic streng hs of 1, 3 and 6 at 298.2 K. The experimental data were regressed by Harned's Rule formalism as follows,

$$\log \gamma_{\pm}(\text{NaCl}) = \log \gamma_{\pm}^{o}(\text{NaCl}) - \alpha_{12}I_{2}$$

In the calculations of the mean activity coefficient, the calibration slope value of S=25.20 mv was used. Lanier used the Nernstian slope value of S=25.69 mv. Figures (7.1) to (7.3) show the logarithm of the mean activity coefficient of NaCl versus the ionic strength of NaNO₃ at total ionic strength one, three and six and 298.2 K. Table (7.1) shows the Harned's coefficients, α_{12} , obtained by the present experiments and the coefficients reported by Lanier. As one can see the values differ slightly in the

third significant figure. Following Harned and Owen [65] the results were reported with only three significant figures for the present experiments. This is consistent with the reproducibility of the present results. It should be mentioned that there are some important differences between Lanier's experiment and the present study. Lanier in his measurements used an Ag/AgCl (second kind electrode) as a reference electrode and in the present experiments a Cl-ISE was used as a reference electrode. An Orion sodium glass Ross electrode was used in the present study but Lanier used a Na glass electrode from Beckman. Lanier in his calculation of the mean activity coefficient of NaCl in the mixed salt solution used the difference of the potential between test solution and saturated binary NaCl solution. In the present experiments, as shown in eq. (7.14), the difference of potential between the test solution and the binary NaCl solution at the same total ionic strength of the mixture was used. As a minor detail even the experimental techniques were observed to be different. In this work for each experiment the stock solution for a specified total ionic strength was prepared separately. While Lanier initially prepared the concentrated stock solutions for both salts and then diluted the solutions to obtain solutions of total ionic strength one and three. Although we believe that Lanier introduced error by neglecting the interference of nitrate ions towards the Cl-ISE, the same path for the sake of comparison of results was followed. Finally, it is worth noticing that the my meter used in measurements has a precision of ± 0.1 mv. As shown by the calculations of the mean activity coefficient, a difference of ± 0.01 mv in the emf values causes the Harned's coefficient to change in its third significant figure. All the experimental emf data for the ternary system $NaCl-NaNO_3-H_2O$ measured in this work are reported in Appendix B.

In conclusion, the emf experiments were successfully carried out for NaCl-NaNO₃-H₂O system and the results obtained for Harned's coefficients are comparable to Lanier's results in spite of the different laboratory procedures, different electrodes, different supplies of chemicals, etc.

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Figure 7.1: Mean ionic activity coefficient of NaCl in aqueous solutions of NaCl and NaNO₃ at I=1 and 298.2 K.

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Figure 7.2: Mean activity coefficient of NaCl in aqueous solutions of NaCl and NaNO₃ at I=3 and 298.2 K.

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Figure 7.3: Mean activity coefficient of NaCl in aqueous solutions of NaCl and NaNO₃ at I=6 and 298.2 K.

Table 7.1: Harned's coefficient, α_{12} , for the ternary system NaCl-NaNO₃-H₂O at 298.2 K.

Total Ionic Strength	I=1	I=3	I=6
α_{12} (present study)	0.035	0.038	0.032
α_{12} (Lanier)	0.0370	0.0336	0.035

7.4 The Mean Activity Coefficient of NaBr in an Aqueous Solutions of NaBr and NaNO₃

For the measurement of the mean activity coefficient of NaBr in the ternary aqueous solution of NaBr and NaNO₃ the following cell was set up.

Detector Electrode	Ternary Solution	Reference Electrode
	$NaBr(I_1)$	Bromide-ISE
Na-ISE	$NaNO_3$ (I ₂)	Single Junction Electrode
		Double Junction Electrode

where $I_1 = m_1$ and $I_2 = m_2$ are the ionic strengths of NaBr and NaNO₃ in the ternary mixture, respectively.

Initially, the experiment was started with the binary of NaBr solution at $I=I_1+I_2$. The potential of the Na-ISE was monitored against Br-ISE, and the single and the double junction reference electrodes. Both the single and double junction electrodes were used to check the validity of the measurements with the Br-ISE as a reference electrode. Using the Nikolsky-Eisenman equation, the emf of the Na-ISE towards the Br-ISE as a reference electrode for the binary NaBr solution can be written as.

$$E^{o}(\text{NaBr}) = E'(\text{NaBr}) + S \ln a^{o}(\text{NaBr})$$
(7.15)

where:

$$a^{\circ}(\mathrm{NaBr}) = [m^{\circ}(\mathrm{NaBr})\gamma^{\circ}_{\pm}(\mathrm{NaBr})]^{2}$$
(7.16)

$$m^{\circ}(\text{NaBr}) = I = I_1 + I_2 = I(\text{NaBr}) + I(\text{NaNO}_3)$$

and S=25.465 mv, as obtained by the calibration described in the previous chapter.

After adding $NaNO_3$ solution of the same total ionic strength as the ternary solution, the potential of the Na-ISE towards the Br-ISE in the ternary mixture is

$$E(\text{NaBr}) = E'(\text{NaBr}) + S \ln a(\text{NaBr})$$
(7.17)

where:

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$$a(NaBr) = I_1(I_1 + I_2)\gamma_{\pm}^2(NaBr)$$
(7.18)

Subtracting eq. (7.16) from (7.17), one then obtains

$$a(\text{NaBr}) = a^{\circ}(\text{NaBr}) exp[\frac{E(\text{NaBr}) - E^{\circ}(\text{NaBr})}{S}]$$
(7.19)

where $a^{\circ}(NaBr)$ is the activity of NaBr in a binary NaBr-H₂O solution of the total ionic strength *I*. By substituting eqs (7.16) and (7.18) in (7.19), one readily obtains

$$\gamma_{\pm}(\text{NaBr}) = \sqrt{\frac{I}{I_1}} \gamma_{\pm}^{\circ}(\text{NaBr}) exp[\frac{E(\text{NaBr}) - E^{\circ}(\text{NaBr})}{2S}]$$
(7.20)

or

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$$\ln \gamma_{\pm}(\text{NaBr}) = \ln \gamma_{\pm}^{o}(\text{NaBr}) + \ln \sqrt{\frac{I}{I_{1}}} + \frac{E(\text{NaBr}) - E^{o}(\text{NaBr})}{2S}$$
(7.21)

Eq. (7.21) was used to calculate the logarithm of the mean activity coefficient of NaBr from emf measurements. The measurements in the ternary aqueous system of NaBr

and NaNO₃ have been carried out at 298.2 K over the range of total ionic strength 0.3 to 6. All the original emf mv data and the numerical results of the reduction of the data are shown in Appendix B. Figures (7.4) to (7.11) show the change of the logarithm of the mean activity coefficient of NaBr versus the ionic strength of NaNO₃ at various total ionic strengths. As the figures show, the behavior of logarithm of the mean ionic activity coefficient respect to the ionic strength of NaNO₃ is linear for all the mixtures of constant total ionic strength studied here. Therefore one can fit the experimental points by the Harned's Rule as:

$$\ln \gamma_{\pm}(\text{NaBr}) = \ln \gamma_{\pm}^{o}(\text{NaBr}) - \alpha_{12}^{\prime}I_{2}$$
(7.22)

All the experimental data were regressed by linear regression analysis. The results for Harned's coefficients, regression coefficient and number of experimental points for each experiment are shown in Table (7.2).

The trace mean activity coefficient of NaBr in the ternary system NaBr-NaNO₃- H_2O can be calculated using the following equation

$$\ln \gamma_{\pm}^{tr}(\text{NaBr}) = \ln \gamma_{\pm}^{o}(\text{NaBr}) - \alpha_{12}^{\prime}I$$
(7.23)

which can be obtained from eq. (7.22) by substituting $I_2 = I$. As explained in Chapter 6, the data can also be fitted by the following expression

$$\ln \gamma_{\pm}(\text{NaBr}) = \ln \gamma_{\pm}^{tr}(\text{NaBr}) + \alpha_{12}^{\prime}I_1$$
(7.24)

which can be obtained by combination of eqs (7.22) and (7.23). Equation (7.24) is very useful since it facilitates the comparison of the mean activity coefficient of NaBr in ternary and binary systems. Figure (7.12) and Table (7.3) show this comparison. The straight lines were produced by eq. (7.24) for various total ionic strengths and the square symbols show the logarithm of the mean activity coefficient of NaBr in the binary mixture NaBr-H₂O. The straight lines are drawn through the corresponding binary points at the same total ionic strengths. This kind of behavior was



Figure 7.5: Mean activity coefficient of NaBr in aqueous solutions of NaBr and NaNO₃ at I=0.5 and 298.2 K.

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Figure 7.7: Mean activity coefficient of NaBr in aqueous solutions of NaBr and NaNO₃ at I=2 and 298.2 K.

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Figure 7.9: Mean activity coefficient of NaBr in aqueous solutions of NaBr and NaNO₃ at I=4 and 298.2 K.

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Figure 7.11: Mean activity coefficient of NaBr in aqueous solutions of NaBr and NaNO₃ at I=6 and 298.2 K.

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، هر. در Table 7.2: Harned's coefficients α'_{12} and α'_{21} for aqueous solutions of NaBr and NaNO₃ at various total ionic strengths and 298.2K.

	$\ln \gamma_{\pm}(\text{NaBr}) = \ln \gamma_{\pm}^{o}(\text{NaBr}) - \alpha_{12}^{\prime}I_{2}$							
	$\ln \gamma_{\pm}(\text{NaNO}_3) = \ln \gamma_{\pm}^o(\text{NaNO}_3) - \alpha_{21}^\prime I_1$							
Total Ionic Strength	1=0 3	I=0 5	I=1	I=2	I=3	I=4	I=5*	I=6
α' ₁₂	0 166	0 164	0 090	0.118	0.127	0 127	0 121	0 124
α ₂₁	-0 081	-0 060	-0 120	-0 083	-0 075	-0 076	-0 082	-0 075
$\alpha'_{12} + \alpha'_{21}$	0 085	0 104	-0 030	0 035	0 051	0 051	0 039	0 049
correlation coefficient x 100	99 71	99 67	99 74	99 79	99 92	99 95	99 91	99 95
No of Observations	26	22	22	28	25	24	25	21
Standard error of α'_{12}	0 002	0 002	0 001	0 001	0 001	0 001	0 001	0 001

* For 1=5, measurements were made with a different Br-ISE as explained in this section

also observed to be the characteristic of hydrochloric acid in halide solutions [65]. From Table (7.2), one can see that within the accuracy of the present measurements, Harned's coefficient α'_{12} is virtually constant at total ionic strengths higher than two. At lower ionic strengths the value of α'_{12} decreases and it presents a minimum in the region of total ionic strength one with an increase at lower ionic strengths. The fact that at low ionic strengths α'_{12} increases and at high ionic strengths it levels off, has also been observed for other ternary systems such as HCl in CsCl, KCl, NaCl, etc [65]. It would have been desirable to repeat experiments to confirm the presence of a minimum of α'_{12} as a function of *I*. However, experiments started from the high concentration regions and three Br-ISE's were damaged before reliable values could be obtained. Measurements with a new (different) electrode can, sometimes, produce variations as shown in Table (7.2). Thus, the question whether or not there is a minimum remains unanswered.



Figure 7.12: Comparison of mean ionic activity coefficient of NaBr in binary aqueous solution of NaBr and in ternary aqueous solutions of NaBr and NaNO₃ at various total ionic strengths and 298.2 K.

Table 7.3: Comparison of the mean ionic activity coefficient of NaBr in a binary aqueous solution of NaBr and in ternary aqueous solutions of NaBr and NaNO₃ at various total ionic strengths and 298.2 K.

n	Bin	ary (Exp)	Γ		7	ernary (l	legressio	n)		_
molality	γ_{\pm}	$\ln(\gamma_{\pm})$	ĺ	$\ln(\gamma_{\pm})$						
NaBr	I=6	I= 6	I=6	I=5	I=4	I=3	I=2	[=1	I=0.5	I=0 3
0 001	0 965	-0 036	-0 513	-0 525	-0.578	-0.578	-0 553	-0.467	-0.444	-0 376
0 002	0 952	-0 049	-0.513	-0 525	-0 578	-0 578	-0.552	-0 467	-0 443	-0.376
0 005	0 928	-0 075	-0 512	-0.524	-0.578	-0 578	-0 552	-0 466	-0.443	-0.375
0 010	0 903	-0 102	-0 512	-0 524	-0.577	-0.577	-0 5 52	-0 466	-0 442	-0 374
0 0 2 0	0 873	-0 136	-0 511	-0 523	-0 576	-0 576	-0 5 50	-0 465	-0.440	-0 373
0 050	0 824	-0 194	-0 507	-0.519	-0 572	-0 572	-0.547	-0.462	-0 436	-0 368
0:00	0 783	-0 245	-0 501	-0 513	-0 566	-0.566	-0.541	-0 458	-0 427	-0 360
0 200	0 742	-0 298	-0 488	-0 501	-0 553	-0 553	-0 529	-0 449	-0.411	-0 343
0 300	0 720	-0 329	-0 476	-0 489	-0 540	-0 540	-0.517	-0.44	-0.395	-0 326
0 100	0 706	-0 348	-0 464	-0 477	-0 528	-0 528	-0 505	-0 43*	-0 378	
0 500	0 697	-0 361	-0 451	-0 465	-0 515	-0.515	-0 194	-0.422	-0 362	
0 600	0 6 92	-0 368	-0 439	-0 453	-0 502	-0 502	-0.482	-0 413		
0 700	0 688	-0 374	-0 427	-0 441	-0 490	-0.490	-0 479	-0 404		
0 800	0 687	-0 375	-0 414	-0 429	-0 477	-0 477	-0 458	-0 395		
0 900	0 686	-0 377	-0.402	-0 416	-0.464	-0 464	-0 447	-0 386		
1 000	0 687	-0 375	-0 389	-0 404	-0 452	-0 452	-0 435	-0 377		
1 200	0 691	-0 370	-0 365	-0 380	-0 426	-0 426	-0 411			
1 400	0 697	-0 361	-0 340	-0 356	-0 401	-0 401	-0 388			
1 600	0 706	0 348	-0 315	-0 332	-0.376	-0 376	-0 364			
1 800	0 717	-0 333	-0 291	-0 308	-0 350	-0 350	-0 340			
2 000	0.730	-0 315	-0 266	-0 284	-0 325	-0 325	-0 317			
2 500	0 768	-0 264	-0 204	-0 223	-0 261	-0 262				
3 000	0 816	-0 203	-0 142	-0 163	-0 198	-0.199				
3 500	0 871	-0 138	-0 081	-0 103	-0 135					
4 000	0 934	-0 068	-0 019	-0 042	-0 071					
4 500	1 005	0 005	0 043	0 018						
5 000	1 083	0 080	0 105	0 078						
5 500	1 169	0156	0 167							
6 000	1 261	0 232	0 228							

7.5 The Mean Activity Coefficient of NaNO₃ in Aqueous Solutions of NaBr and NaNO₃

Initially an attempt was made to measure the emf of the Na-ISE with reference to the NO_3 -ISE or to monitor the potential of the NO_3 -ISE against double junction electrode so that the mean activity coefficient of NaNO₃ could be obtained directly. However it was observed that the data collected was not reproducible, *i.e.*, the emf data obtained starting from the binary system of NaBr and using NaNO₃ as titrant was different from the data obtained with NaBr as titrant starting from the NaNO₃ binary system. In other words, it was concluded that the NO₃-ISE was not reversible in the

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ternary NaBr-NaNO₃- H_2O system. Therefore, following the discussion presented in Chapter 6, the mean activity coefficient of NaNO₃ was calculated using the Gibbs-Duhem equation and Harned's Rule.

As discussed in Chapter 6, if the activity coefficient of one of the salts follows Harned's Rule, one can calculate the Harned's coefficient, α'_{21} , for the second salt by the use of the equation

$$\alpha_{21}' = \alpha_{12}' + \frac{2}{I^2} \int_0^I I \, d \, \ln[\frac{\gamma_{\pm}^o(\text{NaNO}_3)}{\gamma_{\pm}^o(\text{NaBr})}]$$
$$= \alpha_{12}' + \frac{2}{I} [\phi^o(\text{NaNO}_3) - \phi^o(\text{NaBr})]$$
(7.25)

Following Chapter 6, and also discussed by Harned [65], the validity of eq. (7.25) is determined by the accuracy of the linear variation of the logarithm of the mean activity coefficients of the electrolytes at constant total ionic strengths. Thus Harned's Rule should be valid for both salts in order to apply equation (7.25). On the other hand Harned's Rule will be satisfied for the second salt if the following relation is valid.

$$\alpha_{12}' + \alpha_{21}' = \text{constant} \tag{7.26}$$

To test the validity of this equation, α'_{12} is obtained by regression of the experimental data. As discussed by Åkerlöf and Thomas [65], α'_{21} can be evaluated assuming that ratio of mean ionic activity coefficients of the salts in the respective binaries is linear at high total ionic strengths. As shown by Figure (7.13), the ratio of mean activity coefficients for the binaries NaBr-H₂O and NaNO₃-H₂O at high ionic strengths can be written as:

$$\ln \frac{\gamma_{\pm}^{\circ}(\text{NaNO}_{3})}{\gamma_{\pm}^{\circ}(\text{NaBr})} = -K'I$$
(7.27)



Figure 7.13: Logarithm of the ratio of the mean ionic activity coefficient of NaNO₃ and NaBr in binaries at the same ionic strength of the ternary system at 298.2 K.

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Substituting eq. (7.27) in (7.25) one readily obtains:

$$\alpha_{12}' - \alpha_{21}' = K' \tag{7.28}$$

by combining eqs (7.27) and (7.28)

$$(\alpha'_{21} - \alpha'_{12})I = \ln \frac{\gamma^{\circ}_{\pm}(\text{NaNO}_3)}{\gamma^{\circ}_{\pm}(\text{NaBr})}$$
(7.29)

One can also write the Harned's relations for $NaNO_3$ as

$$\ln \gamma_{\pm}(\text{NaNO}_3) = \ln \gamma_{\pm}^{\circ}(\text{NaNO}_3) - \alpha_{21}^{\prime} I_1$$
(7.30)

and

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$$\ln \gamma_{\pm} (\text{NaNO}_3) = \ln \gamma_{\pm}^{tr} (\text{NaNO}_3) + \alpha_{21}^{\prime} I_2$$
(7.31)

The trace mean activity coefficient of NaNO₃ can also be obtained by substituting of $I_1 = I$ in eq. (7.30),

$$\ln \gamma_{\pm}^{tr}(\text{NaNO}_3) = \ln \gamma_{\pm}^{o}(\text{NaNO}_3) - \alpha_{21}^{\prime}I$$
(7.32)

subtracting eq. (7.23) from eq. (7.32) yields:

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$$\ln \frac{\gamma_{\pm}^{tr}(\text{NaNO}_3)}{\gamma_{\pm}^{tr}(\text{NaBr})} = \ln \frac{\gamma_{\pm}^{o}(\text{NaNO}_3)}{\gamma_{\pm}^{o}(\text{NaBr})} - (\alpha_{21}^{\prime} - \alpha_{12}^{\prime})I$$
(7.33)

Substituting eq (7.29) in (7.33) one readily obtains the following relation between the trace activity coefficients:

$$\ln \gamma_{\pm}^{tr}(\text{NaNO}_3) = \ln \gamma_{\pm}^{tr}(\text{NaBr})$$
(7.34)

Total Ionic Strength	$\ln \gamma^{tr}_{\pm}(\mathrm{NaBr})$	$\ln \gamma^{tr}_{\pm}(\mathrm{NaNO}_3)$
0.3	-0.376	-0.382
0.5	-0.444	-0.451
1	-0.467	-0.486
2	-0.553	-0.572
3	-0.578	-0.603
4	-0.578	-0.592
5	-0.525	-0.550
6	-0.513	-0.539

Table 7.4: The activity coefficient of trace electrolytes in the NaBr-NaNO₃-H₂O system at 298.2 K.

Therefore if the ratio of the mean activity coefficients in the binaries is linear, the mean activity coefficients of trace electrolytes in the solution are equal. The Harned's coefficient, α'_{21} , can be calculated either by eq. (7.28) at high ionic strengths, where the ratio of the mean ionic activity coefficients in the binaries is linear, or using eq. (7.25) by the difference of the osmotic coefficients of salts over whole range of ionic strengths. To have consistent results, the osmotic coefficients of the salts reported by Robinson and Stokes [116] were used to calculate the values of α'_{21} which are shown in Table (7.2). As is evident in Table (7.2), at high concentration of the salts in the mixture, α'_{12} does not change significantly with the total ionic strengths of the solutions and equation (7.26) is satisfied within experimental error. Table (7.4) shows the trace mean activity coefficient of NaBr and NaNO₃ at various total ionic strengths of the mixture. These increativity coefficients were calculated using eqs (7.23) and (7.32) and, to a reasonable degree, satisfy eq. (7.34).

Recapitulating, the emf cell technique was used to obtain experimental data for the mean activity coefficient of NaBr in the ternary system NaBr-NaNO₃-H₂O. Harned's coefficient, α'_{12} , was calculated by regression analysis and α'_{21} was evaluated using eq. (7.25). Activity coefficients of the trace salts were computed and it was found that both activity coefficients of the trace electrolytes are nearly equal. As

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indicated by Harned and Owen [65], all these results indicate that the linear variation of $\ln \gamma_{\pm}$ as expressed by Harned's equations, is a good first approximation and can be utilized in the treatment of many mixtures.

With the above elements in mind, errors and drift can be discussed. Experimental errors in the measurements come from various sources. One of the most important sources of uncertainty comes from the precision of the millivolt (mv) measurements. As discussed by Harned [65], for 1-1 Halide mixtures, errors in the emf of $\pm 0.1, \pm 0.2$ and ± 0.2 mv at total ionic strength 0.5, 1 and 3 m, respectively, cause an error in α'_{12} almost equal to $\pm 0.01, \pm 0.01$ and ± 0.005 (based on the natural logarithm) at these ionic strengths. Thus, the errors are more pronounced at ionic strengths less than unity. Although it is difficult to estimate the errors, the consistency of the results shows that for the present measurements an accuracy in α'_{12} of ± 0.005 at high ionic strengths and ± 0.01 at low ionic strengths may be obtained. The accuracy of α'_{21} is less certain so that one may expect an error of ± 0.01 for high ionic strengths and ± 0.02 for low ionic strengths.

Another source of error is the electrode drift Following Freiser's discussion [47], the drift in ISE's can usually be categorized as one of three types (1) A parallel drift characterized by a shift of the calibration line for an electrolyte system in which the slope of the line does not change. (2) A concentration-dependent drift occurs when the slope of the calibration line changes. "for example, one might observe a negative emf drift at high concentration and a positive drift at low concentration Normally, the drift results in a decrease in the slope of the calibration line indicating a degradation in the electrode response (sub-Nernstian)." This effect is most commonly observed with liquid ISE's. Fortunately in the measurements of $NaBr-NaNO_3-H_2O$ system, this kind of drift is not applicable. (3) A random drift characterized by the absence of a regular trend, *i.e.*, non-uniform both in the direction and magnitude of the drift. This kind of drift usually happens with the electrodes which are used many times, particularly at high concentrations. It is impossible to correct this type of drift reliably and the use of a brand new electrode is required. It should be mentioned that in the present measurements three Br-ISE's were used. Using a new electrode needs a new calibration. Moreover, a new electrode has different lot number and it may have a different asymmetry potential. Temperature fluctuations, an unstable liquid junction,

excessive cell resistance, non-equilibrium state of the system, pressure variations, etc are examples of other causes of potential drift. In dilute mixtures drifts are more pronounced because the equilibrium potential will be approached more slowly.

In the present experiments pure deionized water was used to prepare the stock solutions. In some cases it was forced to use different lot numbers of reagent salts and this may result in errors in the comparison of the experimental results. Also, sample calculations showed that within the precision of the mv meter (± 0.1) used in this work, the third decimal place of α'_{12} is only approximate.

Following Harned [65], in a ternary system with a common ion, the following relations are valid, if the assumption of specific ionic interaction of Brönsted is true, for the ternary system.

$$\alpha_{12}' + \alpha_{21}' = 0 \tag{7.35}$$

$$\ln \gamma_{\pm 1}^{tr} = \ln \gamma_{\pm 2}^{tr} \tag{7.36}$$

Although for the present system the activity coefficients of the trace electrolytes are almost equal, α'_{12} is not equal to $-\alpha'_{21}$ as it can be seen from Table (7.2). This may be due to experimental errors discussed above or it may suggest that the theory of Brönsted, which leads to the result that the sum of Harned's coefficients is zero, is not strictly valid due to the effect of the third ion.

7.6 The Mean Activity Coefficient of NaBr in an Aqueous Solutions of NaBr and $Ca(NO_3)_2$

The ternary system NaBr-Ca(NO₃)₂-H₂O consists of four different ions so that the same information on the system can also in principle be obtained from the ternary system NaNO₃-CaBr₂-H₂O. However the p₁eparation of the mixture from NaBr and Ca(NO₃)₂ is easier than from NaNO₃ and CaBr₂, because CaBr₂ is a very hygroscopic material and is difficult to prepare with high purity. In fact, a mixture of these four ions results in four mean ionic activity coefficients as follows:

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$$\gamma_{\pm} (\text{NaBr}) = (\gamma_{\text{Na}} \gamma_{\text{Br}})^{1/2}$$
(7.37)

$$\gamma_{\pm}(\text{Ca}(\text{NO}_3)_2) = (\gamma_{\text{Ca}}\gamma_{\text{NO}_3}^2)^{1/3}$$
(7.38)

$$\gamma_{\pm}(\text{NaNO}_3) = (\gamma_{\text{Na}}\gamma_{\text{NO}_3})^{1/2}$$
(7.39)

$$\gamma_{\pm}(\text{CaBr}_2) = (\gamma_{\text{Ca}}\gamma_{\text{Br}}^2)^{1/3}$$
(7.40)

All four mean activity coefficients are not independent and are related by the following equation

$$\frac{\gamma_{\pm}^{4}(\text{NaNO}_{3})}{\gamma_{\pm}^{4}(\text{NaBr})} = \frac{\gamma_{\pm}^{3}(\text{Ca}(\text{NO}_{3})_{2})}{\gamma_{\pm}^{3}(\text{CaBr}_{2})}$$
(7.41)

Therefore knowing three mean activity coefficients, one can obtain the fourth from eq. (7.41). Nevertheless it is practically impossible to measure the activities of the Ca^{++} and NO_3^- ions due to the interference of nitrate ions with the Ca-ISE as discussed in Chapter 6 and the irreversibility of the NO₃-ISE response as shown in the previous section. Thus, the only choice is to measure the mean ionic activity coefficient of NaBr as it was performed for the NaBr-NaNO₃-H₂O system. However the measurements were limited to high ionic strengths in which the selectivity coefficient of Na-ISE towards Ca⁺⁺ ions is very low. Using the cell arrangement described in Chapter 6, one can write the same equation as obtained for the NaBr-NaNO₃-H₂O system, i_{Ca} .

$$a(\text{NaBr}) = a^{o}(\text{NaBr}) exp[\frac{E(\text{NaBr}) - E^{o}(\text{NaBr})}{S}]$$
(7.42)

where:

$$a^{\circ}(\mathrm{NaBr}) = [I\gamma_{\pm}^{\circ}(\mathrm{NaBr})]^{2}$$
(7.43)

$$a(\text{NaBr}) = [I\gamma_{\pm}(\text{NaBr})]^2$$
(7.14)

By substituting eqs (7.43) and (7.44) in (7.42) and taking logarithms, one obtains.

$$\ln \gamma_{\pm}(\text{NaBr}) = \ln \gamma_{\pm}^{o}(\text{NaBr}) + \ln \frac{I}{I_{1}} + \frac{E(\text{NaBr}) - E^{o}(\text{NaBr})}{2S}$$
(7.45)

The emf data measurements were reduced using eq. (7.45) in order to evaluate the logarithm of mean activity coefficient of NaBr in the NaBr-Ca(NO₃)₂-H₂O system. Figures (7.14) to (7.16) show the logarithm of the mean activity coefficient of NaBr in the ternary system at total ionic strengths 3, 4.5 and 6 and 298.2 K. The numerical results are presented in Appendix C. As before, the data were fit by linear regression and Harned's model was used as follows:

$$\ln \gamma_{\pm}(\text{NaBr}) = \ln \gamma_{\pm}^{o}(\text{NaBr}) - \alpha_{12}^{\prime}I_{2}$$
(7.46)

where

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$$I_2 = 3 \,\mathrm{m}(\mathrm{Ca}(\mathrm{NO}_3)_2) \tag{7.47}$$

Table (7.5) shows the result of Harned's rule. As one can see this model properly fit the data at total ionic strengths 3 to 6. The trace activity coefficient of the NaBr can be obtained as

$$\ln \gamma_{\pm}^{\prime r} (\text{NaBr}) = \ln \gamma_{\pm}^{o} (\text{NaBr}) - \alpha_{12}^{\prime} I$$
(7.48)

where

$$I = m(NaBr) + 3m(Ca(NO_3)_2)$$
(7.49)

One can also write:

$$\ln \gamma_{\pm} (\text{NaBr}) = \ln \gamma_{\pm}^{\prime r} (\text{NaBr}) + \alpha_{12}^{\prime} I_1$$
(7.50)



Figure 7.14: Mean activity coefficient of NaBr in aqueous solutions of NaBr and Ca(NO₃)₂ at I=3 and 298.2 K.



Figure 7.15: Mean activity coefficient of NaBr in aqueous solutions of NaBr and Ca(NO₃)₂ at I=4.5 and 298.2 K.



Figure 7.16: Mean activity coefficient of NaBr in aqueous solutions of NaBr and Ca(NO₃)₂ at I=6 and 298.2 K.

$\ln \gamma_{\pm}(\mathrm{NaBi}) = \ln \gamma_{\pm}^{o}(\mathrm{NaBr}) - \alpha_{12}^{\prime}I_{2}$				
Total Ionic Strength	I=3	I=4.5	I=6	
α'12	0.090	0.095	0.107	
$\ln \gamma^o_{\pm}(\mathrm{NaBr})$	-0.199	0.010	0.233	
correlation coefficient x 100	99.70	99.95	99.90	
No. of Observations	23	24	25	
Standard error of α'_{12}	0.001	0.001	0.001	

Table 7.5: Harned's coefficients α'_{12} for the mean ionic activity coefficients of NaBr in aqueous solutions of NaBr and Ca(NO₃)₂ at various total ionic strengths and 298.2 K.

The trace activity coefficient of NaBr can be evaluated by either eq. (7.48) or eq. (7.50).

7.7 The Mean Activity Coefficient of $Ca(NO_3)_2$ in Aqueous Solutions of NaBr and $Ca(NO_3)_2$

It was initially assumed that Harned's Rule also applies for $C_{\partial}(NO_3)_2$ so that, using eq. (6.36), the following equation should hold,

$$2\alpha'_{12} + \alpha'_{21} = \text{constant} \tag{7.51}$$

However equation (7.51) is not valid. Then, higher order coefficients were used

$$\ln \gamma_{\pm 2} = \ln \gamma_{\pm 2}^{\circ} - \alpha_{12}^{\prime} I_1 - \beta_{21}^{\prime} I_1^2$$
(7.52)

where:

$$\gamma_{\pm 2} = \gamma_{\pm} (\operatorname{Ca}(\operatorname{NO}_3)_2)$$
$$\gamma_{\pm 2}^{\circ} = \gamma_{\pm}^{\circ} (\operatorname{Ca}(\operatorname{NO}_3)_2)$$

Following the discussion of Chapter 6 and using eqs (6.43) and (6.45), one readily writes:

$$\alpha'_{21} + \beta'_{21}I = \frac{1}{I}\ln\frac{\gamma^o_{\pm 2}}{(\gamma^o_{\pm 1})^2} + \frac{2}{I}\int_0^I \alpha'_{12}dI$$
(7.53)

$$\alpha_{21}' = \frac{d}{dI} \ln \frac{\gamma_{\pm 2}^o}{(\gamma_{\pm 1}^o)^2} + 2I \frac{\partial \alpha_{12}'}{\partial I} + 2\alpha_{12}'$$
(7.54)

As explained in Chapter 6, the limits of the line $\alpha'_{21} + \beta'_{21}I_1$ at $I_1=0$ and $I_1=I$ can be calculated by eqs (7.54) and (7.53) respectively. Having two points of this line, one can calculate the slope to find the value of β'_{21} provided that the function $\alpha'_{21} + \beta'_{21}I_1$ is a linear function. Then eq. (6.42) can be used to get values of $\alpha'_{21} + \beta'_{21}I_1$ at different values of I_1 . One needs the values of α'_{12} at low total ionic strength so that eq (6.42) can be used. However these values of α'_{12} are not available at low ionic strengths and they can not be obtained by extrapolation because α'_{12} may change more rapidly with the total ionic strength in dilute solutions. One alternative is to assume that the function is linear and evaluate the slope by two points at $I_1=0$ and $I_1=I$. Harned's coefficients, α'_{12} , can then be expressed by linear equation

$$\alpha_{12}' = 0.0724 + 0.0056 I \tag{7.55}$$

Figure (7.17) shows the ratio of the mean activity coefficient of NaBr and $Ca(NO_3)_2$ in their respective binaries that can be correlated by the following relation.

$$\ln \frac{\gamma_{\pm 2}^{\circ}}{(\gamma_{\pm 1}^{\circ})^2} = -0.1104 - 0.3463 I + 0.2704\sqrt{I}$$



Figure 7.17: Logarithm of the ratio of the mean activity coefficient of $Ca(NO_3)_2$ and the square mean activity coefficient of NaBr in the respective binary solutions at the same ionic strength of the ternary system at 298.2 K.

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Table (7.6) was constructed using eqs (7.53) and (7.54). As one can see from Table (7.6), the first order Harned's Rule is not enough to approximate the mean activity coefficient of $Ca(NO_3)_2$ because eq. (7.51) is not valid. For $Ca(NO_3)_2$, using eq. (6.34), the following equation for the ternary system $Ca(NO_3)_2$ -NaBr-H₂O should be satisfied.

$$2\alpha'_{12} + \alpha'_{21} + 2I\beta'_{21} \simeq \text{constant}$$

$$(7.56)$$

Table 7.6: Harned's coefficients α'_{21} and β'_{21} for the mean ionic activity coefficient of $Ca(NO_3)_2$ in aqueous solutions of NaBr and $Ca(NO_3)_2$ at various total ionic strengths and 298.2 K

Total Ionic Strength	α'21	$2\alpha'_{12} + \alpha'_{21}$	$\alpha_{21}' + \beta_{21}' I$	β'_{21}	$2\alpha_{12}' + \alpha_{21}' + 2I\beta_{21}'$
3	-0.054	0.127	-0.064	-0.004	0 106
4.5	-0.042	0.148	-0.073	-0.007	0.085
6	-0.009	0.205	-0.076	-0.011	0 072

Although from Table (7.6) it is possible to detect a trend in the value of the sum given by eq. (7.56), as an approximation within the experimental error the sum can be considered as constant. The - of more coefficients is not justified with the accuracy of our measurements. As one can see from Table (7.6) one might also conclude that β'_{21} approaches zero at lower ionic strengths, *i.e.*, that the Ca(NO₃)₂ follows Harned's Rule at very low total ionic strengths. Following the discussion of errors in the previous section, the results show that for the present measurements one may expect an accuracy in α'_{12} of ± 0.005 and in α'_{21} of ± 0.01 at high ionic strengths.

If eq. (7.56) is assumed valid, the activity coefficient of trace $Ca(NO_3)_2$ can then be evaluated by the following equation.

$$\ln \gamma_{\pm 2}^{tr} = \ln \gamma_{\pm 2}^{o} - \alpha_{21}^{\prime} I - \beta_{21}^{\prime} I^{2}$$
(7.57)

The activity coefficients of both trace electrolytes in ternary system NaBr-Ca(NO₃)₂- H_2O are shown in Table (7.7).

Table 7.7: The activity coefficient of trace electrolytes in the NaBr-Ca(NO₃)₂-H₂O system at 298.2 K.

Total Ionic Strength	$\ln \gamma_{\pm}^{tr}(NaBr)$	$\frac{\ln \gamma_{\pm}^{tr}(\mathrm{Ca}(\mathrm{NO}_3)_2)}{}$
3	-0.475	-0.887
4.5	-0.423	-0.754
6	-0.412	-0.608

7.8 Synopsis

In conclusion, in this chapter the selectivity coefficients of nitrate, sodium and calcium ISE's were determined by separate solution technique. It was found that Br-ISE does not interfere with the other ions and it was observed that the selectivity coefficient of Na-ISE can be neglected, particularly at high concentrations of interfering ions. The experimental emf data were reduced for three ternary system, NaCl-NaNO₃-II₂O, NaBr-NaNO₃-II₂O and NaBr-Ca(NO₃)₂-H₂O. The mean activity coefficients of NaCl and NaBr in these ternary systems were obtained by the emf cells using ISE's. The Harned's coefficient, α'_{12} , for these ternary systems were evaluated by linear regression analysis of the experimental data. The Harned's coefficients, α'_{21} , for NaBr-NaNO₃-H₂O system was calculated using the Gibbs-Duhem equation. It was observed that the mean activity coefficient of calcium nitrate in the NaBr-Ca(NO₃)₂-H₂O system does not follow Harned's Rule. A second order correction, β'_{21} , was used for mean activity coefficient of calcium nitrate and both coefficients, α'_{21} and β'_{21} , were evaluated using Maxwell's relations of the mean activity coefficients of NaBr and Ca(NO₃)₂.

Chapter 8

A Novel Mixing Rule for Multicomponent Electrolyte Solutions

Models for binary electrolyte systems reviewed in Chapter 3 are extended to multicomponent aqueous electrolyte mixtures [136]. The models which have been most widely used for ternary systems are the Meissner [92] and the Pitzer [103, 104,105,106] models. We will not elaborate on the use of these models here. In this chapter, a new Harned's Rule formulation will be discussed and the NLTL-NRF model will be extended for ternary systems using suitable mixing rules for NRF mean activity coefficients.

8.1 Modelling Harned's Coefficient

Harned's Rule, as discussed in Chapter 6, can be written as:

$$\ln \gamma_{\pm 1} = \ln \gamma_{\pm 1}^{o} - \alpha_{12}^{\prime} I_2 \tag{8.1}$$

and
$$\ln \gamma_{\pm 1}^{tr} = \ln \gamma_{\pm 1}^{o} - \alpha_{12}^{\prime} I \tag{8.2}$$

As discussed in Chapter 7, most aqueous electrolyte ternary systems obey Harned's Rule. Thus having an estimate of Harned's coefficients would permit the use of the Harned's expression to approximate the mean activity coefficient data in ternary electrolyte systems. If the activity coefficient of the trace electrolyte in the mixture is available, using eq. (8.2) Harned's coefficient, α'_{12} , is obtained as

$$\alpha_{12}' = \frac{\ln \gamma_{\pm 1}^o - \ln \gamma_{\pm 1}^{tr}}{I}$$
(8.3)

By combining eqs (8.1) and (8.3), one can readily obtain

$$\ln \gamma_{\pm 1} = \ln \gamma_{\pm 1}^{o} - \frac{I_2}{I} (\ln \gamma_{\pm 1}^{o} - \ln \gamma_{\pm 1}^{tr})$$
(8.4)

From where, we obtain the limits

$$I_1 \rightarrow I ; I_2 \rightarrow 0$$
 then $\ln \gamma_{\pm 1} \rightarrow \ln \gamma_{\pm 1}^{\circ}$

$$l_1 \to 0; l_2 \to I$$
 then $\ln \gamma_{\pm 1} \to \ln \gamma_{\pm 1}^{tr}$

Thus relation (8.3) gives the correct limiting behavior for a ternary system which follows Harned's Rule. Therefore having the activity coefficient of the trace electrolyte allows the calculation of the Harned's coefficient from data of the binary systems.

8.2 The Extension of the NRTL-NRF Model to Ternary Systems

As discussed in Chapter 4, using NRTL-NRF model the mean activity coefficient of electrolyte "ij" in a multicomponent system can be written as:

$$\ln \gamma_{\pm ij} = \ln(\gamma_{\pm ij})_{DH} + \ln(\gamma_{\pm ij})_{NRF}$$
(8.5)

where $\ln(\gamma_{\pm ij})_{DH}$ is considered to be an extended Debye-Hückel form common to all electrolytes,

$$\ln(\gamma_{\pm ij})_{DH} = Z_i Z_j f(I) \tag{8.6}$$

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$$f(I) = \frac{-A\sqrt{I}}{1+B\sqrt{I}}$$
(8.7)

For a ternary aqueous system which consists of two salts, the first formed by ions 1 and 2 and the second by ions 3 and 4, the mean activity coefficient of each of the electrolytes in the respective binary solutions of a single electrolyte in water at the same total ionic strength I can be written as

$$\ln \gamma_{\pm 12}^{o} = Z_1 Z_2 f(I) + \ln(\gamma_{\pm 12}^{o})_{NRF}$$
(8.8)

$$\ln \gamma^{o}_{\pm 34} = Z_3 Z_4 f(I) + \ln(\gamma^{o}_{\pm 34})_{NRF}$$
(8.9)

Multiplying eq. (8.8) by Z_3Z_4 and eq. (8.9) by Z_1Z_2 and subtracting, one readily obtains

$$\ln \frac{(\gamma_{\pm 12}^{o})^{Z_3 Z_4}}{(\gamma_{\pm 34}^{o})^{Z_1 Z_2}} = \ln \frac{(\gamma_{\pm 12}^{o})^{Z_3 Z_4}_{NRF}}{(\gamma_{\pm 34}^{o})^{Z_1 Z_2}_{NRF}}$$
(8.10)

After a detailed consideration of the mixing rules available in the literature [64,92] and some systematic trials, we postulate the following mixing rule to obtain NRTL-NRF mean activity coefficient for electrolyte 1 or 12.

$$\ln(\gamma_{\pm 12})_{\rm NRF} = \ln(\gamma_{\pm 12}^{\circ})_{\rm NRF} - \frac{K_2}{2} [Y(3) \ln \frac{(\gamma_{\pm 12}^{\circ})_{\rm NRF}^{Z_3 Z_2}}{(\gamma_{\pm 32}^{\circ})_{\rm NRF}^{Z_1 Z_2}} + Y(4) \ln \frac{(\gamma_{\pm 12}^{\circ})_{\rm NRF}^{Z_1 Z_4}}{(\gamma_{\pm 14}^{\circ})_{\rm NRF}^{Z_1 Z_2}}] (8.11)$$

where $K_2=1$ if the ternary system has a common cation (ion 1, $\gamma_{\pm 12}^o = \gamma_{\pm 32}^o$) or common anion (1on 2, $\gamma_{\pm 12}^o = \gamma_{\pm 14}^o$) and $K_2=2$ if the ternary system is without a common ion. Here odd numbers stand for cations and even numbers for anions. When a single number follows the symbol γ_{\pm} it refers to the electrolyte or salt and when two numbers follow (one odd and one even) they refer to the ions forming the salt. Thus $\gamma_{\pm 1} = \gamma_{\pm 12}$ and $\gamma_{\pm 2} = \gamma_{\pm 34}$. In addition, we define,

$$Y(3) = \frac{\nu_2^+ m_2 Z_3^2}{2I}$$

$$Y(4) = \frac{\nu_2^- m_2 Z_4^2}{2I}$$

where by convention the numbers following in parenthesis refer to an ion and not to a salt. The exponents $Z_t Z_j$ of eq. (8.11) were suggested by the form of eq. (8.10).

A similar equation can be written for the other electrolytes For example, the NRF mean activity coefficient of electrolyte 2 formed by ions 3 and 4 is written as

$$\ln(\gamma_{\pm 34})_{\rm NRF} = \ln(\gamma_{\pm 34}^{\circ})_{\rm NRF} - \frac{K_1}{2} [Y(1) \ln \frac{(\gamma_{\pm 34}^{\circ})_{\rm NRF}^{Z_1 Z_4}}{(\gamma_{\pm 14}^{\circ})_{\rm NRF}^{Z_3 Z_4}} + Y(2) \ln \frac{(\gamma_{\pm 34}^{\circ})_{\rm NRF}^{Z_3 Z_2}}{(\gamma_{\pm 32}^{\circ})_{\rm NRF}^{Z_3 Z_4}}] \quad (8.12)$$

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$$Y(1) = \frac{\nu_1^+ m_1 Z_1^2}{2I}$$
$$Y(2) = \frac{\nu_1^- m_1 Z_2^2}{2I}$$

Similarly $K_1=1$ if the ternary system has a common cation (ion 3, $\gamma_{\pm 34}^o = \gamma_{\pm 14}^o$) or a common anion (ion 4, $\gamma_{\pm 34}^o = \gamma_{\pm 32}^o$) and $K_1=2$ if the ternary system is without a common ion. For the ternary system $NaBr(1)-NaNO_3(2)-H_2O(3)$ formed by ions $Na^+(1)$, $Br^-(2)$ and $NO_3^-(4)$ in which $Z_1=Z_2=Z_4=1$ and $Y(4)=Y_2=I_2/I$; eq. (8.11) is simplified as follows

$$\ln(\gamma_{\pm 1})_{\rm NRF} = \ln(\gamma_{\pm 1}^{o})_{\rm NRF} - \frac{1}{2} Y_2 [\ln \frac{(\gamma_{\pm 1}^{o})_{\rm NRF}}{(\gamma_{\pm 2}^{o})_{\rm NRF}}]$$
(8.13)

where 1 stand for NaBr and 2 for NaNO₃. Thus eq. (8.10), for all binaries of the type 1-1/1-1, 2-2/2-2 and even for 1-2/1-2 systems, is written as:

$$\ln \frac{\gamma_{\pm 1}^{o}}{\gamma_{\pm 2}^{o}} = \ln \frac{(\gamma_{\pm 1}^{o})_{\text{NRF}}}{(\gamma_{\pm 2}^{o})_{\text{NRF}}}$$
(8.14)

As one can see from eq. (8.6), the Debye-Hückel mean activity coefficients of both salts in a ternary system are equivalent to Debye-Hückel mean a divity coefficients of the salts in the binaries at the same total ionic strength as the ternary system Then, subtracting eq. (8.8) from (8.5)

$$\ln \gamma_{\pm 1} = \ln \gamma_{\pm 1}^{\circ} + \left[\ln(\gamma_{\pm 1})_{\rm NRF} - \ln(\gamma_{\pm 1}^{\circ})_{\rm NRF} \right]$$
(8.15)

Substituting eq. (8.13) in (8.15) and using the relation (8.14), one readily obtains

$$\ln \gamma_{\pm 1} = \ln \gamma_{\pm 1}^{\circ} - \frac{I_2}{2I} \ln \frac{\gamma_{\pm 1}^{\circ}}{\gamma_{\pm 2}^{\circ}}$$
(8.16)

 \neg_{i} . (8.16) gives the mean activity coefficient of electrolyte 1 in the ternary system using binary data only. The activity coefficient of trace salt 1 can be obtained from eq. (8.16) when I_2 approaches I.

$$\ln \gamma_{\pm 1}^{tr} = \frac{1}{2} (\ln \gamma_{\pm 1}^{o} + \ln \gamma_{\pm 2}^{o})$$

or

$$\gamma_{\pm 1}^{tr} = (\gamma_{\pm 1}^{o} \gamma_{\pm 2}^{o})^{1/2} \tag{8.17}$$

On the other hand by substituting the activity coefficient of trace electrolyte, *i.e*, eq. (8.17), into eq. (8.3) one obtains Harned's coefficient as:

$$\alpha_{12}' = \frac{1}{2I} \ln \frac{\gamma_{\pm 1}^2}{\gamma_{\pm 2}^2} \tag{8.18}$$

Therefore using eq. (8.17) for the trace activity coefficient of electrolyte "1" results in the same form of Harned's Rule if we either use the Harned's coefficient given by eq. (8.3) or if we use the NRTL-NRF model, *i.e.*, eq. (8.18).

Similarly for electrolyte 2 one readily obtains:

$$\gamma_{\pm 2}^{tr} = (\gamma_{\pm 1}^{o} \gamma_{\pm 2}^{o})^{1/2} \tag{8.19}$$

$$\alpha_{21}' = \frac{1}{2I} \ln \frac{\gamma_{\pm 2}^o}{\gamma_{\pm 1}^o}$$
(8.20)

Therefore for 1-1/1-1 ternary systems, using eqs (8.17), (8.18), (8.19) and (8.20) one obtains

$$\gamma_{\pm 1}^{tr} = \gamma_{\pm 2}^{tr}$$
 (8.21)

$$\alpha_{12}' + \alpha_{21}' = 0 \tag{8.22}$$

Harned and Robinson [64], using the Brönsted theory for the mean activity coefficients of salts, obtained the relation given by eq. (8.17) for the trace mean activity coefficient of salts in 1-1/1-1 electrolyte ternary systems. Meissner and Kusik [92] proposed a mixing rule for the reduced mean activity coefficient of salts and obtained eq. (8.17) for the mean activity coefficient of trace electrolytes.

Similarly for a ternary system with common anion $(Z_2=1)$ and two cations $(Z_1=1,Z_3=2)$ eq. (8.11) can be written as:

$$\ln(\gamma_{\pm 1})_{\rm NRF} = \ln(\gamma_{\pm 1}^{\circ})_{\rm NRF} - \frac{1}{3} Y_2 \left[\ln \frac{(\gamma_{\pm 1}^{\circ})_{\rm NRF}^2}{(\gamma_{\pm 2}^{\circ})_{\rm NRF}} \right]$$
(8.23)

and eq. (8.10) takes the form

$$\ln \frac{(\gamma_{\pm 1}^{o})^{2}}{\gamma_{\pm 2}^{o}} = \ln \frac{(\gamma_{\pm 1}^{o})_{\rm NRF}^{2}}{(\gamma_{\pm 2}^{o})_{\rm NRF}}$$
(8.21)

By substituting eq (8.24) in (8.23), the NRF mean activity coefficient of electrolyte 1 can be expressed as

$$\ln(\gamma_{\pm 1})_{\rm NRF} = \ln(\gamma_{\pm 1}^{o})_{\rm NRF} - \frac{1}{3}Y_2 \ln \frac{(\gamma_{\pm 1}^{o})^2}{\gamma_{\pm 2}^{o}}$$
(8.25)

Using eqs (8.5), (8.6) and (8.25)

$$\ln \gamma_{\pm 1} = Z_1 Z_2 f(I) + \ln(\gamma_{\pm 1}^o)_{\text{NRF}} - \frac{1}{3} Y_2 \ln \frac{(\gamma_{\pm 1}^o)^2}{\gamma_{\pm 2}^o}$$
(8.26)

The mean activity coefficient of electrolyte 1 in its binary aqueous solution at the same total ionic strength as the ternary system can be written as

$$\ln \gamma_{\pm 1}^{\circ} = Z_1 Z_2 f(I) + \ln(\gamma_{\pm 1}^{\circ})_{\rm NRF}$$
(8.27)

Subtracting eq. (8.27) from (8.26) and using $Y_2 = I_2/I$.

$$\ln \gamma_{\pm 1} = \ln \gamma_{\pm 1}^{\circ} - \frac{I_2}{3I} \ln \frac{(\gamma_{\pm 1}^{\circ})^2}{\gamma_{\pm 2}^{\circ}}$$
(8.28)

When $I_2=I$, then the trace mean activity coefficient of electrolyte 1 is readily obtained as

$$\gamma_{\pm 1}^{t\tau} = (\gamma_{\pm 1}^{o} \gamma_{\pm 2}^{o})^{1/3} \tag{8.29}$$

and, using eq (8.28), Harned's coefficient, α'_{12} , can be written as

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$$\alpha'_{12} = \frac{1}{3I} \ln \frac{(\gamma^{o}_{\pm 1})^2}{\gamma^{o}_{\pm 2}} = \frac{1}{I} (\ln \gamma^{o}_{\pm 1} - \ln \gamma^{tr}_{\pm 1})$$
(8.30)

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Using a similar approach, the same form of equations (8.29) and (8.30) can be obtained for a ternary system with common cation $(Z_1=1)$ and two anions $(Z_2=1, Z_4=2)$. For a ternary system without a common ion and involving a bivalent ion, such as an aqueous solution of NaBr and Ca(NO₃)₂, one can use the same approach starting from eqs (8.11) and (8.12). The expressions for the trace mean activity coefficients of salts in the ternary system NaBr-Ca(NO₃)₂-H₂O will be developed in the next sections

8.2.1 New Harned's Formulation for Ternary Systems with a Common Ion

Having the mean activity coefficient of the trace electrolyte by eq. (8.17) permits the use of eq. (8.3) or (8.18) to evaluate Harned's coefficient α'_{12} for ternary systems with a common ion. Using eq. (8.3), the formal Harned's coefficient used in literature which uses the base ten logarithm instead of the natural logarithm can be written as:

$$\alpha_{12} = \frac{\alpha'_{12}}{\ln(10)} = \frac{\ln \gamma^{\circ}_{\pm 1} - \ln \gamma^{\prime r}_{\pm 1}}{2.303/}$$
(8.31)

$$\log \gamma_{\pm 1}^{tr} = \frac{\ln \gamma_{\pm 1}^{tr}}{2.303} \tag{8.32}$$

Table (8.1) shows the values of Harned's coefficients and activity coefficients of trace NaCl evaluated by eqs (8.31), (8.32) and (8.17) for various uni-univalent ternary systems with a common ion. As one can see from Table (8.1), the calculated values of trace activity coefficient and Harned's coefficient, α_{12} , of NaCl in the ternary system NaCl-NaNO₃-H₂O are in excellent agreement with experimental data within experimental error. The calculated results for the ternary systems NaCl-NaC₂H₃O₂-H₂O and NaCl NaClO₄-H₂O at low ionic strength (I=1) are very close to the experimental data. However at high ionic strength one can observe a difference between the experimental and the calculated values of the trace activity coefficient and the

Table 8.1: Comparison of the trace mean activity coefficient of NaCl and Harned's coefficient, α_{12} , for uni-univalent electrolyte ternary systems^{*}.

Ternary	Total lonic	$\log \gamma^{tr}_{\pm}(\text{NaCl})$		α ₁₂	
System	Strength(I)	Exp	Calc	Exp	Calc
NaCl	1	-0.158	-0 152	-0 02 1	0.030
& $NaC_2H_3O_2$	3	-0.112	-0 077	-0 011	-0.023
NaCl	1	-0.219	-0.221	0 0.37	0.039
&	3	-0 247	-0 253	0.0.34	0.035
NaNO3	6	-0.216	-0.218	0.035	0.035
NaCl	1	-0 182	-0 192	0.000	0.010
&	3	-0155	-0.180	0.003	0.011
NaClO ₄	6	-0 066	-0.087	0.010	0.01.3

 \star The experimental data were reported by Lamer [83]

Harned's coefficient of NaCl. Table (8.2) shows the results of trace activity coefficient and Harned's coefficient for other ternary systems with a common ion calculated using eqs (8.29) and (8.30) As Table (8.2) shows, the calculated results at low ionic strength are very close to the experimental data. For example, the calculated trace activity coefficient and the Harned's coefficient of NaCl in aqueous solutions of NaCl and a 2-1 electrolyte with common ion Cl^- are in excellent agreement with experimental data at an ionic strength one. At high ionic strengths there is a difference between the calculated and experimental data. The deviations between calculated and experimental values at high ionic strengths may be due to inaccurate binary or ternary data or perhaps the invalidity of the Brönsted theory at high ionic strengths in ternary systems. This theory was used as a guide in the derivation of Harned's Rule and also as a base for the NRTL-NRF model. The experimental binary data which were taken from the tabulation of Robinson and Stokes [116], are shown by Table (8.3).

Ternary	Total Ionic	$\log \gamma_{\pm}^{tr}$	$\log \gamma^{tr}_{\pm}(\mathrm{NaCl})$		12
System	Strength(I)	Exp	Calc	Exp	Calc
NaCl	1	-0.243	-0.230	0.061	0.048
&	3	-0.307	-0.279	0 054	0.042
Na ₂ SO ₁	6	-0.306	-0.272	0.050	0.044
NaC'l	1	-0.168	-0.168	-0.015	-0 014
&	3	-0.115	-0.130	-0.010	-0 005
MgCl ₂	6	0.030	0.005	-0.006	-0.002
NaCl	1	-0.178	-0.175	-0.004	-0.007
&:	3	-0.140	-0.149	-0.002	0 001
CaCl ₂	6	-0.014	-0.036	0.001	0 005
NaCl	1	-0.182	-0.180	0.000	-0 002
&	3	-0.152	-0.160	0.002	0.005
SrCl ₂	6	-0.042	-0059	C 006	0.009
NaCl	1	-0.190	-0.187	0.007	0.005
&	3	-0.187	-0 181	0 013	0.012
BaCl ₂	6	-0.153	-0 137	0.019	0.013

Table 8.2: Comparison of the trace mean activity coefficient of NaCl and Harned's coefficient, α_{12} , for non uni-univalent electrolyte ternary systems*.

* The experimental data were reported by Lanier [83]

Table 8.3: Experimental mean activity coefficients of various salts in binary aqueous solutions at 298.15K. (the values for NaCl at I=5 are $\log \gamma_{\pm 1}^o = -0.058$ and for BaCl₂ at I=5, $\log \gamma_{\pm 2}^o = -0.352$)

Binary	$\log \gamma^o_{\pm}$			
Solution	I=1	l=3	I=6	
NaCl	-0.182	-0.146	-0.006	
$NaC_2H_3O_2$	-0.121	-0.008	-	
Na ₂ SO ₄	-0.509	-0.690	-0.811	
NaNO ₃	-0.261	-0.360	-0.431	
NaClO4	-0.201	-0.214	-0.169	
MgCl ₂	-0.323	-0.245	-0 022	
CaCl ₂	-0.344	-0.301	-0.101	
SrCl ₂	-0.357	-0.333	-0.171	
BaCl ₂	-0.379	-0.397		

8.2.2 The Rule for Aqueous Solutions of NaBr and NaNO₃

Using eqs (8.17), (8.18) and (8.20), the trace activity coefficient of NaBr and NaNO₃ in the ternary system NaBr-NaNO₃-H₂O can be written as:

$$\ln \gamma_{\pm}^{tr}(\text{NaBr}) = \ln \gamma_{\pm}^{tr}(\text{NaNO}_3) = \frac{1}{2} \ln(\gamma_{\pm}^o(\text{NaBr})\gamma_{\pm}^o(\text{NaNO}_3))$$
(8.33)

$$\alpha_{12}' = -\alpha_{21}' = \frac{1}{2I} \ln \frac{\gamma_{\pm}^{o}(\text{NaB}^{\cdot})}{\gamma_{\pm}^{o}(\text{NaNO}_{3})}$$
(8.34)

Eq. (8.34) can be manipulated to obtain the following relations.

$$\alpha_{12}' + \alpha_{21}' = 0 \tag{8.35}$$

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$$\alpha'_{21} - \alpha'_{12} = \frac{1}{I} \ln \frac{\gamma^{e}_{\pm}(\text{NaNO}_{3})}{\gamma^{e}_{\pm}(\text{NaBr})}$$
(8.36)

As one can see, eq. (8.36) is equivalent to eq. (7.29) which was obtained for the case when the logarithm of the ratio of mean activity coefficients of the binary solutions was linear with respect to I. Table (8.4) shows the experimental and the calculated values of trace mean activity coefficient and Harned's coefficient, α'_{12} , of NaBr. Similarly Table (8.5) shows the results for NaNO₃. As one can see from both tables the activity coefficient of trace electrolytes at low ionic strengths are close to the experimental values within experimental error. However at high ionic strengths the deviation from experimental values becomes larger. Following the specific ionic interaction theory of the Brönsted, the trace activity coefficient calculated by eq. (8.33) is for low ionic strengths. For high ionic strengths the Brönsted theory is not valid so that the geometric mean of activity coefficient of pure binaries may not be suitable for the calculation of the activity coefficient of the trace salts.

The NRTL-NRF model, eq. (8.11), is based on the specific ionic interaction of the Brönsted which means that there are no interactions between the ionic species of the same sign. In this case, as was discussed previously, the sum of Harned's coefficients is zero and the activity coefficient of trace electrolytes are equal. The model was used for different ternary systems. In fact, the model works perfectly for some 1-1/1-1 ternary systems such as NaCl-NaNO₃-H₂O for which the sum of Harned's coefficients are actually zero. However as can be seen from Table (7.2), the sum of the coefficients are not zero for the NaBr-NaNO₃-H₂O system although the sum are almost constant. The difference between experimental and calculated α'_{12} and α'_{21} is almost ± 0.02 at high ionic strengths. There are two ways of interpreting this difference, the first one is that the ternary system NaBr-NaNO₃-H₂O does not follow the Brönsted theory. The second is that there is a possibility of systematic experimental error in the experiments. As discussed in previous section, the accuracy of our experiments was ± 0.1 mv. To get more precise results and answer this question one would need an accuracy of $\pm .01$ mv.

Total Ionic	$\ln \gamma^o_{\pm}(\mathrm{NaBr})$	$\ln \gamma^{tr}_{\pm}(NaBr)$		$\ln \gamma^{o}_{\pm}(\mathrm{NaBr}) = \ln \gamma^{\mathrm{tr}}_{\pm}(\mathrm{NaBr})$		a	r' ₁₂
Strength	Exp	Ехр	Calc	Exp	Calc		
0.3	-0.329	-0.376	-0.367	0.166	0.130		
0.5	-0.361	-0.444	-0.421	0.164	0.120		
1	-0.375	-0.467	-0.488	0.090	0.112		
2	-0.315	-0.553	-0.526	0.118	0.106		
3	-0.203	-0.578	-0.516	0.127	0.104		
4	-0.068	-0.578	-0.482	0.127	0.104		
5	0.080	-0.525	-0.436	0.121	0.103		
6	0.232	-0.513	-0.378	0.124	0.102		

Table 8.4: Comparison of the trace mean activity coefficient of NaBr and Harned's coefficient, α'_{12} , for aqueous solutions of NaBr and NaNO₃

Table 8.5. Comparison of the trace mean activity coefficient of NaNO₃ and Harned's coefficient, α'_{21} , for aqueous solutions of NaBr and NaNO₃

Total Ionic	$\ln \gamma^{\circ}_{\pm}(\mathrm{NaNO}_3)$	$\ln \gamma^{tr}_{\pm}(\text{NaNO}_3)$		$1\gamma_{\pm}^{\circ}(NaNO_3)$ $\ln \gamma_{\pm}^{\prime r}(NaNO_3)$		a	21
Strength	Exp	Exp	Calc	Exp	Calc		
0.3	-0.406	-0.382	-0.367	-0.081	-0.130		
0.5	-0.481	-0.451	-0.421	-0.060	-0.120		
1	-0.600	-0 486	0.488	-0.120	-0.112		
2	-0.738	-0.572	-0.526	-0.083	-0.106		
3	-0.828	-0.603	-0.516	-0.075	-0.104		
4	-0.896	-0.592	-0.482	-0.076	-0.104		
5	- 0.952	-0.550	-0.436	-0.082	-0.103		
6	0.989	-0.539	-0.378	-0.075	-0.102		

8.2.3 The Rule for Aqueous Solutions of NaBr and $Ca(NO_3)_2$

Using eqs (8.11) and (8.12) for ternary system NaBr-Ca(NO_3)₂-H₂O, one can readily obtain

$$\ln(\gamma_{\pm 1})_{\rm NRF} = \ln(\gamma_{\pm 1}^{\circ})_{\rm NRF} - \frac{1}{3}Y_2 \ln \frac{(\gamma_{\pm 1}^{\circ})_{\rm NRF}}{(\gamma_{\pm 3}^{\circ})_{\rm NRF}} - \frac{2}{3}Y_2 \ln \frac{(\gamma_{\pm 1}^{\circ})_{\rm NKF}^2}{(\gamma_{\pm 4}^{\circ})_{\rm NRF}}$$
(8.37)

where:

$$\gamma_{\pm 1} = \gamma_{\pm 12} = \gamma_{\pm} (\text{NaBr})$$

$$\gamma_{\pm 2} = \gamma_{\pm 34} = \gamma_{\pm}(\mathrm{Ca}(\mathrm{NO}_3)_2)$$

 $\gamma_{\pm 3} = \gamma_{\pm 14} = \gamma_{\pm}(\text{NaNO}_3)$

$$\gamma_{\pm 4} = \gamma_{\pm 32} = \gamma_{\pm} (\text{CaBr}_2)$$

and the superscript o indicates the mean activity coefficient of the salts in the binary system. Similarly the NRF mean activity coefficient of $Ca(NO_3)_2$ can be written as:

$$\ln(\gamma_{\pm 2})_{\rm NRF} = (\gamma_{\pm 2}^{\circ})_{\rm NRF} - Y_1 \ln \frac{(\gamma_{\pm 2}^{\circ})_{\rm NRF}}{(\gamma_{\pm 4}^{\circ})_{\rm NRF}} - \frac{1}{2} Y_1 \ln \frac{(\gamma_{\pm 2}^{\circ})_{\rm NRF}}{(\gamma_{\pm 3}^{\circ})_{\rm NRF}^2}$$
(8.38)

By substituting eq. (8.37) in (8.5) and using eq. (8.6), one obtains

$$\ln \gamma_{\pm 1} = Z_1 Z_2 f(I) + \ln(\gamma_{\pm 1}^{\circ})_{\text{NRF}} - \frac{1}{3} Y_2 \ln \frac{(\gamma_{\pm 1}^{\circ})_{\text{NRF}}}{(\gamma_{\pm 3}^{\circ})_{\text{NRF}}} - \frac{2}{3} Y_2 \ln \frac{(\gamma_{\pm 1}^{\circ})_{\text{NRF}}^2}{(\gamma_{\pm 4}^{\circ})_{\text{NRF}}}$$
(8.39)

Writing the equations for binaries which are at the same total ionic strength as the ternary system and using a similar approach to the one used in the previous section, eq. (8.39) takes the following form:

$$\ln \gamma_{\pm 1} = \ln \gamma_{\pm 1}^{\circ} - \frac{1}{3} Y_2 \ln \frac{\gamma_{\pm 1}^{\circ}}{\gamma_{\pm 3}^{\circ}} - \frac{2}{3} Y_2 \ln \frac{(\gamma_{\pm 1}^{\circ})^2}{\gamma_{\pm 4}^{\circ}}$$
(8.40)

Thus, eq (8.40) can be used to evaluate the mean activity coefficient of NaBr in ternary system NaBr-Ca(NO₃)₂-H₂O. The trace mean activity coefficient of NaBr in this ternary system can readily obtained by replacing $Y_2 = 1$ as:

$$\ln \gamma_{\pm 1} = \ln \gamma_{\pm 1}^{\circ} - \frac{1}{3} \ln \frac{\gamma_{\pm 1}^{\circ}}{\gamma_{\pm 3}^{\circ}} - \frac{2}{3} \ln \frac{(\gamma_{\pm 1}^{\circ})^2}{\gamma_{\pm 4}^{\circ}}$$

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$$\gamma_{\pm 1}^{tr} = \left[\frac{\gamma_{\pm 3}^{\circ} \gamma_{\pm 4}^{\circ 2}}{\gamma_{\pm 1}^{\circ 2}}\right]^{1/3}$$
(8.41)

Although the mixture was prepared from NaBr and Ca(NO₃)₂, the trace mean activity coefficient of NaBr appears to be related also to the mean activity coefficient of NaNO₃ and CaBr₂ in their respective binaries. One can readily write the Harned's coefficient, α'_{12} , from eq. (8.40) as:

$$\alpha_{12}' = \frac{1}{3I} \ln \frac{\gamma_{\pm 1}^{o}}{\gamma_{\pm 3}^{o} \gamma_{\pm 4}^{o}}^{2} = \frac{1}{I} (\ln \gamma_{\pm 1}^{o} - \ln \gamma_{\pm 1}^{tr})$$
(8.42)

Similarly by using eq. (8.38), the mean activity coefficient of $Ca(NO_3)_2$ can be written as

$$\ln \gamma_{\pm 2} = \ln \gamma_{\pm 2}^{o} - Y_1 \ln \frac{\gamma_{\pm 2}^{o}}{\gamma_{\pm 4}^{o}} - \frac{1}{2} Y_1 \ln \frac{\gamma_{\pm 2}^{o}}{(\gamma_{\pm 3}^{o})^2}$$
(8.43)

thus, the trace activity coefficient of $Ca(NO_2)_2$ can be written as:

$$\gamma_{\pm 2}^{tr} = \frac{\gamma_{\pm 4}^{o} \gamma_{\pm 3}^{o}}{(\gamma_{\pm 2}^{o})^{1/2}}$$
(8.44)

and by using eq. (8.43) the Harned's coefficient, α'_{21} , can be written as:

$$\alpha_{21}' = \frac{1}{I} \ln \frac{(\gamma_{\pm 2}^{\circ})^{3/2}}{\gamma_{\pm 4}^{\circ} \gamma_{\pm 3}^{\circ}} = \frac{1}{I} [\ln \gamma_{\pm 2}^{\circ} - \ln \gamma_{\pm 2}^{tr}]$$
(8.45)

As is evident, using the mixing rule, i.e, eq. (8.12), does not lead to higher order correction for the mean activity coefficient of $Ca(NO_3)_2$. In the other words, the mixing rules, i.e. eqs (8.11) and (8.12), are appropriate if both salts follow Harned's Rule.

Table (8.6) shows the comparison of the experimental trace mean activity coefficient of NaBr and the calculated values using eq. (8.41). Also the Harned's coefficient, α'_{12} , was calculated by eq. (8.42) and compared with the experimental values. As one can observe the calculated values are in excellent agreement with the experimental data within experimental error. The experimental values of the mean activity coefficient of electrolytes in binary solutions are shown in Table (8.7)

Table 8.6: Comparison of the trace mean activity coefficient of NaBr and Ilarned's coefficient, α'_{12} , for aqueous solutions of NaBr and Ca(NO₃)₂

Total Ionic	$\ln \gamma_{\pm}^{tr}(\text{NaBr})$		α'12		
Strength	Exp	Calc	Ехр	Calc	
3	-0.475	-0.485	0.090	0.094	
4.5	-0.423	-0.464	0.095	0.104	
6	-0.412	-0.409	0.107	0.107	

Similarly the trace activity coefficient of $Ca(NO_3)_2$ can be calculated by eq. (8.44) and the Harned's coefficient, α'_{21} , by eq. (8.45). As Table (8.8) shows, the calculated values of trace activity coefficient of calcium nitrate and Harned's coefficient, α'_{21} , are close to the experimental values at total ionic strength three. However at higher ionic strengths the calculated values deviate from the experimental data because $Ca(NO_3)_2$ does not follow Harned's Rule. As explained in the end of Chapter 7, it seems that $Ca(NO_3)_2$ follows Harned's Rule at low ionic strengths and that the NRF mixing rule is applicable for ternary systems in which both salts follow Harned's Rule.

Ionic Strength	$\ln \gamma^{\circ}_{\pm}(\text{NaBr})$	$\ln \gamma^{\circ}_{\pm}[\mathrm{Ca}(\mathrm{NO}_3)_2]$	$\ln \gamma^o_{\pm}(\mathrm{NaNO}_3)$	$\ln \gamma^o_{\pm}(\mathrm{CaBr}_2)$
3	-0.203	-1.085	-0.828	-0.518
4.5	+0.005	-1.085*	-0.926	-0.228*
6	+0.232	-1.058	-0.989	+0.112

Table 8.7: Experimental mean activity coefficients of various salts in binary solutions at 298.15 K (Hamer and Wu, 1972; Robinson and Stokes, 1959).

* obtained by linear interpolation of data

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Table 8.8: Comparison of the trace mean activity coefficient of $Ca(NO_3)_2$ and Harned's coefficient, α'_{21} , for aqueous solutions of NaBr and $Ca(NO_3)_2$

Icnic	$\ln \gamma_{\pm}^{tr}(\mathrm{Ca}(\mathrm{NO}_3)_2)$		α	/ 21
Strength	Exp	Calc	Exp	Calc
3	-0.887	-0.803	-0.054	-0.094
4.5	-0.754	-0.612	-0.042	-0.105
6	-0.603	-0.347	-0.009	-0.119

8.3 Extension of the Rule for Multicomponent Electrolyte Mixtures

Although no experimental evidence is given in this work to support the extension of the model to multicomponent electrolyte systems, for completeness we write here the general equations for a multielectrolyte solution. In general, for a salt (k) or $\binom{1}{2}$ corresponds a cation (2k-1) or i=j-1 and an anion (2k) or j, where j is an even number. The general form for the NRF mean activity coefficient of salt $\binom{1}{2}$ or (ij) can be postulated as

$$\ln(\gamma_{\pm ij})_{\rm NRF} = \ln(\gamma_{\pm ij}^{\circ})_{\rm NRF} - \frac{1}{2} \sum_{(k \neq j/2)} K_k \left\{ Y(2k-1) \ln \left[\frac{(\gamma_{\pm ij}^{\circ})_{\rm NRF}^{Z_{2k-1}Z_{j}}}{(\gamma_{\pm (2k-1)j}^{\circ})_{\rm NRF}^{Z_{k-1}Z_{j}}} \right] + Y(2k) \ln \left[\frac{(\gamma_{\pm ij}^{\circ})_{\rm NRF}^{Z_{i}Z_{j}}}{(\gamma_{\pm i(2k)}^{\circ})_{\rm NRF}^{Z_{i}Z_{j}}} \right] \right\}$$
(8.46)

with

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$$Y(2k-1) = \frac{\nu_k^+ m_k Z_{2k-1}^2}{2I}$$

$$Y(2k) = \frac{\nu_k m_k Z_{2k}^2}{2I}$$

where I is the total ionic strength of the mixture. The salt coefficient K_k is equal to the number of ions of salt k which are different from the ions of salt $(\frac{1}{2})$ under consideration. If both the cation and the anion of salt (k) are the same as the cation and anion of salt $(\frac{1}{2})$, $K_k=0$. In fact, in the case of a ternary system the equation reduces to that of a binary salt system $(\frac{1}{2})/H_2O$ and there is no perturbation by the added salt (k). If salt (k) has a common ion with salt $(\frac{1}{2})$, $K_k=1$. In addition, due to the cancellation of the logarithmic term in the sum, the common ion terms cancel out in this case. Finally, when both ions of salt (k) are different from the ions forming salt $(\frac{i}{2})$, $K_k=2$. The assumption of additivity of effects suggests equation (8.46) should give a good approximation at low total ionic strengths where Harned's Rule applies. For a ternary aqueous system consisting of two salts with mean activity coefficients of $\gamma_{\pm 12}$ and $\gamma_{\pm 34}$, eq. (8.46) reduces to eqs (8.11) and (8.12) respectively.

The mixing rule postulated in this work can be formulated in more general terms. In fact, it is not necessary to make use of the NRTL-NRF contribution to the activity coefficients. In general, combining eqs (8.5) and (8.46)

$$\ln \gamma_{\pm ij} = \ln(\gamma_{\pm ij})_{\rm DH} + \ln(\gamma_{\pm ij}^{o})_{\rm NRF} - \frac{1}{2} \sum_{(k \neq j/2)} K_k \left\{ Y(2k-1) \ln \left[\frac{(\gamma_{\pm ij}^{o})_{\rm NRF}^{Z_{2k-1}Z_j}}{(\gamma_{\pm (2k-1)j}^{o})_{\rm NRF}^{Z_iZ_j}} \right] + \frac{1}{2} \sum_{(k \neq j/2)} K_k \left\{ Y(2k-1) \ln \left[\frac{(\gamma_{\pm ij}^{o})_{\rm NRF}^{Z_{2k-1}Z_j}}{(\gamma_{\pm (2k-1)j}^{o})_{\rm NRF}^{Z_iZ_j}} \right] + \frac{1}{2} \sum_{(k \neq j/2)} K_k \left\{ Y(2k-1) \ln \left[\frac{(\gamma_{\pm ij}^{o})_{\rm NRF}^{Z_{2k-1}Z_j}}{(\gamma_{\pm (2k-1)j}^{o})_{\rm NRF}^{Z_{2k-1}Z_j}} \right] + \frac{1}{2} \sum_{(k \neq j/2)} K_k \left\{ Y(2k-1) \ln \left[\frac{(\gamma_{\pm ij}^{o})_{\rm NRF}^{Z_{2k-1}Z_j}}{(\gamma_{\pm (2k-1)j}^{o})_{\rm NRF}^{Z_{2k-1}Z_j}} \right] + \frac{1}{2} \sum_{(k \neq j/2)} K_k \left\{ Y(2k-1) \ln \left[\frac{(\gamma_{\pm ij}^{o})_{\rm NRF}^{Z_{2k-1}Z_j}}{(\gamma_{\pm (2k-1)j}^{o})_{\rm NRF}^{Z_{2k-1}Z_j}} \right] \right\} \right\}$$

$$Y(2k) \ln \left[\frac{(\gamma_{\pm i}^{\circ})_{\text{NRF}}^{Z_i Z_{2k}}}{(\gamma_{\pm i}^{\circ})_{\text{NRF}}^{Z_i Z_j}}\right]$$

$$(8.47)$$

The two first terms of the right hand side correspond to the binary system of salt ij in water at the same total ionic strength as the system.

Finally, combining equation (8.47) with equations of the form of eq. (8.10), we obtain

$$\ln \gamma_{\pm ij} = \ln \gamma_{\pm ij}^{o} - \frac{1}{2} \sum_{(k \neq j/2)} K_k \left\{ Y(2k-1) \ln \left[\frac{(\gamma_{\pm ij}^{o})^{Z_{2k-1}Z_j}}{(\gamma_{\pm (2k-1)j}^{o})^{Z_iZ_j}} \right] + Y(2k) \ln \left[\frac{(\gamma_{\pm ij}^{o})^{Z_iZ_{2k}}}{(\gamma_{\pm i(2k)}^{o})^{Z_iZ_j}} \right] \right\}$$
(8.48)

Other than noticing the generality of this form, it is important to realize that the prediction of properties of ternary systems presented here involves no adjustable parameters and is based only on experimental data of binaries.

8.4 Synopsis

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In a conclusion. in this chapter, a new Harned's formulation was developed to calculate the Harned's coefficient in ternary systems. The NRTL-NRF model was extended to ternary systems with or without a common ion. Using the NRTL-NRF mixing rule, the expressions for trace mean activity coefficients of electrolytes in ternary systems were obtained. Thus, by having trace activity coefficient values, one can use the new Harned's formulation to calculate Harned's coefficients. Without using trace activity coefficient, The Harned's coefficients can also be directly obtained by the eqs were developed using the NRTL-NRF mixing rules. Finally, the mixing rule was extended to multicomponent electrolyte mixtures so that mean activity coefficients can be directly predicted using data of only binaries.

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Chapter 9

Conclusions, Original Contributions to Knowledge and Suggestions for Future Work

In this chapter original contributions and conclusions described in previous chapters are summarized. Based on the experience gained from this research, some proposals for future work on both modelling and experimental measurements will be discussed.

9.1 Conclusions

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The main conclusions made in this study are presented in the same order in which they have been presented in the main body of the thesis.

9.1.1 A Non-Random Factor Model for the Excess Gibbs Energy of Electrolyte Solutions

A novel excess Gibbs energy function to represent the deviations from ideality of electrolyte solutions was derived on the basis of the assumptions of specific interactions of Brönsted and of local electroneutrality of Chen. The function consists of two contributions, one due to long-range forces, represented by the Debye-Hückel theory, and the other to short-range forces, represented by local composition concept. The new concepts used in construction of the model are the expression of the local compositions in terms of non-random factors (NRF) and the choice of the random fluid as a reference fluid. With only two adjustable parameters per electrolyte, the model is valid for the whole range of electrolyte concentration, from dilute solutions up to saturation. The model was tested to fit mean ionic activity coefficients of electrolytes in binary aqueous solutions at 298.15 K and higher temperatures. Results are compared with those obtained from the one or two parameter models of Meissner, Bromley, Pitzer and Chen et al. . The model presented in this work consistently produces better results, and in particular it reproduces the experimental values from the dilute to saturation regions, the later region being one in which the other models deteriorate. Using the model, the mean activity coefficients of eighty four uni-univalent and eighty non-uni-univalent aqueous binaries at 298.15 K were correlated and the binary parameters reported. Also the model was tested for some binary aqueous electrolyte solutions at various temperatures and results were much better than those obtained with other models.

9.1.2 Experimental Work

An electrochemical cell apparatus using Ion Selective Electrodes (ISE) was designed, constructed and successfully operated to measure the electromotive force (emf) of ions in the aqueous electrolyte mixtures. An ion selective electrode connected to the reference jack of a mv meter so that the electromotive force of an ion could be measured using another ISE as a reference electrode without using conventional reference electrodes. This experimental system is suitable for measuring mean activity coefficients of electrolytes in binary and multicomponent aqueous and non-aqueous mixtures. Using this apparatus, the following experiments were carried out.

- I The following binary aqueous electrolyte solutions were calibrated and the validity of Nernstian equation was investigated.
 - 1. NaBr-H₂O
 - 2. $NaNO_3-H_2O$

3. NaCl-H₂O

- 4. $CaBr_2-H_2O$
- 5. $CaCl_2-H_2O$
- 6. $Ca(NO_3)_2 H_2O$
- II For the ternary system NaCl-NaNO₃-H₂O, emf experiments were performed in order to show the reproducibility of the experimental data and validity of the experimental procedures. Agreements with available data from the literature were good.
- III For the ternary system NaBr-NaNO₃-H₂O, new experimental data of the mean ionic activity coefficient of NaBr were obtained at total ionic strengths 0.3-6 and at 298.15 K.
- IV Experiments for the ternary system $NaBr-Ca(NO_3)_2-H_2O$ (without a common ion) were performed at high ionic strengths and new data for the mean ionic activity coefficient of NaBr at total ionic strengths 3, 4.5 and 6 were obtained.

The mean ionic activity coefficients of NaBr in the ternary systems of NaBr-NaNO₃-H₂O and NaBr-Ca(NO₃)₂-H₂O were correlated by linear regression at various total ionic strengths and Harned's Rule appears to be valid. Keeping the total ionic strength of the mixture constant, the mean activity coefficient of NaNO₃ in NaBr-NaNO₃-H₂O system was evaluated using the Gibbs-Duhem equation and assuming that both salts obey Harned's Rule. Similarly, using the cross differentiation of the mean activity coefficients, the mean activity coefficient of Ca(NO₃)₂ in the NaBr-Ca(NO₃)₂-H₂O system was evaluated and it was found that Ca(NO₃)₂ does not follow Harned's Rule so that a second order correlation was applied.

9.1.3 A Novel Mixing Rule for the Mean Activity Coefficient of Electrolytes in Ternary Systems

A novel mixing rule was proposed for the mean ionic activity coefficient of electrolytes in mixtures in terms of the mean activity coefficients of the electrolytes in binary systems. Using the mixing rule permits the prediction trace mean activity coefficients and the Harned's coefficients of the electrolytes in ternary systems. The rule was extended to multicomponent systems which obey Harned's Rule, although predictions were not tested against experimental data. For the ternary NaBr-Ca(NO₃)₂-H₂O system, using the new mixing rule, the trace mean activity coefficient and Harned's coefficient, α'_{12} , of NaBr were calculated at various total ionic strengths yielding values were in very good agreement with experimental data. The model was also applied to ternary systems with a common ion such as NaBr-NaNO₃-H₂O and CaCl₂-NaCl H₂O and it is suitable for mixtures which follow the Brönsted specific ionic theory. For the NaCl-NaNO₃-H₂O system the calculated trace activity coefficients and the Harned's coefficient, α'_{12} were in excellent agreement with experimental data.

9.2 Original Contributions to Knowledge

9.2.1 Modelling

The following main ideas are considered to be original contributions to knowledge

- The use of the non-random factor concept to model the nonideality of electrolytes solutions taking as a reference the random state. The consideration of the difference between a mixture with local order and a random mixture to obtain the excess Gibbs energy, made the whole difference in the results when compared with other models.
- Expressing the local compositions in terms of non-random factors and writing the NRTL equation in terms of non-random factors results in a new expression for modelling liquid mixtures.
- the development of a mixing rule based on the concept of non-random factors for the short range forces. This mixing rule is based on a detailed study of the characteristics of previously proposed mixing rules and it is, to a large extent, intuitive.

9.2.2 Experimental

- A commercial milivoltmeter was adapted to work using an ISE in place of a reference electrode (SJE or DJE). The repeated measurements using both an ISE and either a SJE or DJE as reference electrode confirmed that both methods give comparable results within the experimental error.
- New experimental data for the mean activity coefficients of the following aqueous solutions were obtained.
 - 1. The mean activity coefficients of NaCl in the NaCl-NaNO₃-H₂O systems were measured at three different ionic strengths and 298.2 K.
 - The mean activity coefficients of NaBr in the NaBr-NaNO₃-H₂O and NaBr-Ca(NO₃)₂-H₂O systems were measured at various ionic strengths and 298.2 K.

9.3 Suggestions for Future Work

Based on experience gained in this project, future work is proposed on both thermodynamic modelling and experimental measurements.

9.3.1 Thermodynamic Modelling

The NRTL-NRF model is a successful model for the excess Gibbs energy of aqueous binary electrolyte solutions. the choice of the random liquid as a reference fluid is a new concept which, through non-random factors, can be applied to non-electrolyte mixtures. For future work, the following fields of the research may be proposed.

1. The NRTL-NRF model may be applied to non-electrolyte solutions using a molecular or a group method. Previous models, such as Wilson and NRTL, have been applied to variety of non-electrolyte solutions for both Vapor-Liquid and Liquid-Liquid Equilibria (LLE). It is worthwhile to apply the NRTL-NRF model to the same mixtures and compare the results with the previous models, particularly for LLE data which the other models can not predict well.

- 2. It was found that the NRTL-NRF model can be extended to multicomponent electrolyte mixtures without using additional adjustable parameters. It is proposed to construct an excess Gibbs energy function for multicomponent electrolyte solutions starting from ionic and molecular species similarly to the treatments developed in Chapter 4 for binaries.
- 3. The NRTL-NRF model can in principle be applied to multisolvent, aqueous and non-aqueous, electrolyte mixtures such as H₂O-CH₃OH-NaCl system.
- 4. The new mixing rule developed in Chapter 8, seems to be successful for ternary aqueous electrolyte mixtures which obey Harned' Rule. By considering non-specific interactions, *i.e.*, the interactions between the same ionic species, the mixing rule may be extended to mixtures which do not follow Harned's Rule.
- 5. Non-random factors are useful for the representation of local composition effects in electrolyte and non-electrolyte solutions. It is worthwhile to investigate this concept further from a statistical thermodynamic point of view.

9.3.2 Future Experimental Work

Foremost, future experimental work for aqueous and non-aqueous electrolyte should involve additional measurements of experimental data, particularly for multicomponent electrolyte solutions. The data available for multicomponent electrolyte solutions, particularly non-aqueous electrolyte solutions, are far from sufficient.

Due to limitations in the use of ion selective electrodes in multicomponent electrolyte solutions, only measurements of the mean ionic activity coefficients of NaBr in both NaBr-NaNO₃-H₂O and NaBr-Ca(NO₃)₂-H₂O systems keeping total ionic strength of the mixture constant were possible. The mean activity coefficient of NaNO₃ and Ca(NO₃)₂ were calculated using the Gibbs-Duhem and Maxwell equations. It is desirable to measure the activity of water which, together with the activity of NaBr obtained using emf, will permit the direct use of the Gibbs-Duhem equation to evaluate the mean ionic activity coefficient of NaNO₃ or Ca(NO₃)₂ in both ternary systems.

A Vapor-Liquid Equilibria apparatus was proposed and partially constructed [62] to measure the vapor pressure of the water in electrolyte solutions in order to

evaluate the activity of the water. The system is based on Van Ness type apparatus which has been widely used for VLE studies of organic mixtures. The apparatus consists of an equilibrium cell, a pressure transducer and an injection piston. The equilibrium cell was constructed from a glass funnel and a glass flask attached to narrow part of the funnel by the use of a clamp connector. Two stainless steel parallel plates keep the funnel tightly. The pressure transducer, vacuum line and solvent input tube are connected to the upper plate. The flask used for multicomponent electrolyte solutions has an one-way value to open and close the flask temporary. The volumetric injection piston can be used to inject the liquid solvent into the previously evacuated cell. The pressure transducer can be used to monitor the equilibrium vapor pressure of the solvent at various concentrations. Thus, a pure reagent salt or a very concentrated electrolyte solution should be previously prepared and degassed. The solution is placed in the glass flask of the cell and after the equilibrium cell has been evacuated and reached to equilibrium, the vapor pressure of the solvent can be monitored by the pressure transducer. The next step is the injection of the solvent to the cell to dilute the solution and again the cell should be reached to equilibrium so that the vapor pressure can be measured at different concentrations of the electrolyte. It should be noted that the pressure transducer should be calibrated with a pure solvent or a binary standard electrolyte solution before starting to carry out any experiment. For more details, one can refer to my proposal [62].

The electromotive force apparatus can be improved in some ways. One of the most important parts of the apparatus is the mv meter, Orion EA 920. This instrument is a good digital meter for measurements of the potential of icns with an accuracy ± 0.1 mv. Most of the meters available in the market have an accuracy ± 0.1 mv that it may be suitable for titration experiments. However for measurements of the activity of the ions to obtain mean ionic activity coefficients, it is advisable to use mv meters with an accuracy of ± 0.01 mv which give more accurate values of the Harned's coefficients. The availability of high precision electrometers permits the designing and building of very precise mv meters with high internal impedance so that the potentials can be monitored with an accuracy of ± 0.01 mv.

Another improvement is to interface the mv meter with a personal computer. The mv meter, EA 920, has a RS-232C serial link output which allows operation

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with computers and other equipment. Thus, by installing a data acquisition system it is possible to measure many data for the same equilibrium point and, by using an averaging program, the best value of the potential at equilibrium can be obtained. One can also investigate the transient response of the ion selective electrodes during measurements. This information is useful in dynamic investigations of ion selective electrodes.

Finally, the apparatus with available ISE's has capability for measuring nonaqueous electrolyte systems such as NaBr-CH₃OH system and for multisolvent electrolyte solutions such as NaCl-H₂O-C₂H₅OH system. Data for these systems can be particularly useful for understanding of liquid-liquid systems of interest in biotechnological separations.

LITERATURE CITED

- [1] Abrams, D. S., Prausnitz, J. M., (1975), AIChE J., 21, 116.
- [2] Ananth, M. S., Ramachandran, S., (1990), AIChE J., <u>36</u>, N. 3, 370.
- [3] Ananthapapadmanabband, K. P., Goddard, E. D., (1987), Langmuir, 3, 25-31.
- [4] Ambrose, D., (1986), IUPAC, "Experimental Thermodynamics", V. 2, Butterworths Scientific Publication, London.
- [5] Anderson, H. C., Chandler D., (1971), J. Chem. Phys. <u>55</u>, 1497.
- [6] Anderson, H. C., Chandler D., (1970), J. Chem. phys. <u>53</u>, 547.
- [7] Arrhenius, S., (1888), Z. Phys. Chem., 1, 481.
- [8] Arrhenius, S., (1887), Z. Phys. Chem., 1, 631.
- [9] Arrhenius, S., (1887), Philos. Mag., <u>26</u>, 81.
- [10] Ball, F-X, Planche, H., Frürst W., Renon H., (1985), AIChE J., <u>31</u>, N. 8, 1233.
- [11] Bard, A. J., Faulkner, L. R., (1980), "Electrochemical Methods", John Wiley & Sons, New York.
- [12] Berboruah, C. P., Covington A. K., Robinson R. A., (1970), J. Chem. Thermodyn., <u>2</u>, 431.
- Bates, R. G., (1989), "Electrochemistry Past and Present", edited by Stock, J. S., Orna, M. V., ACS Symposium Series, <u>195</u>, Washington DC.
- [14] Bates, R. G., Dickson, A. G., (1983), Anal. Chem., 55, N. 8, 1275.
- [15] Bates, R. G., Stables R., Robinson, R. A., (1970), Anal. Chem., <u>42</u>, N. 8, 867.
- [16] Blum, L., (1989), J. Phys. Chem., <u>93</u>, 7478.
- [17] Blum, L., (1987), J. Phys. Chem., <u>92</u>, 2969.

- [18] Blum, L., (1975), J. Mol. Phys., <u>30</u>, 1529.
- [19] Boles, J. H., Buck, R. P., (1973), Anal. 1 Chem., <u>45</u>, N. 12, 2057.
- [20] Bromley, L. A., (1973), AIChE J., 19, N. 2, 313.
- [21] Brönsted, J. N., (1922), J. Amer. Chem. Soc., <u>44</u>, 938.
- [22] Butler, J. N., (1979), "Activity Coefficients in Electrolyte Solutions", V. 1, Edited by Pytkowicz, R. M., CRC Press.
- [23] Butler, J. N., Huston R., (1970), Anal. chem., <u>42</u>, N. 6, 676.
- [24] Butler, J. N., Huston R., (1969), Anal. Chem., <u>41</u>, N. 1, 201.
- [25] Butler, J. N., Huston R., (1967), J. Phys. Chem. 71, N. 13, 4479.
- [26] Cabezas, H. Jr., O'Connell, J. P., (1986), Fluid Phase Equilibria, <u>30</u>, 213.
- [27] Cammann, K., (1979), "Working with Ion-Selective Electrodes", Springer-Verlag, Berlin Heidelberg, New York.
- [28] Card, D. N., Valleau J. P., (1970), J. Chem. Phys., <u>52</u>, N. 12, 6232.
- [29] Cheluget, E. L., (1989), "PhD proposal", Chemical Engineering Department, McGill University, Montreal.
- [30] Chen, C-C, Evans, L. B., (1986), AIChE J. <u>32</u>, 444.
- [31] Chen, C-C, Britt, H., Boston, J. E., Evans, L. B., (1982), AIChE J. 28, 588.
- [32] Christensen, C., Sander, C. B., Fredenslund A., Rasmussen P., (1983), Fluid Phase Equil., <u>13</u>, 297.
- [33] Copeman, T. W., (1987), Fluid Phase Equil., <u>35</u>, 165.
- [34] Copeman, T. W., Stein, F. P., (1986), Fluid Phase Equil., <u>30</u>, 237.
- [35] Covington, A. K., (1979), "Ion-selective Electrode Methodology", V. 1, CRC Press.

- [36] Cruz, J. L., Renon, H., (1978), AIChE J., 24, 817.
- [37] (1989), "Cole-Parmer Catalog".
- [38] Davies, C. W., (1938), J. Chem. Soc., 2093.
- [39] Davies, C. W., (1962), "Ion Association", Butterworths Scientific Publications, London.
- [40] Debye, D., Hückel, E., (1923), Phys. Zeitschrift, 24, 185 and 305.
- [41] Efstathiou, C. E., (1983), Anal. Chim. Acta, <u>154</u>, 41.
- [42] Esteso, M. A., Hernandez-Luis, F. F., Fernandez-Merida, L., Gonzales-Diaz,
 D. M., (1989), J. Sol. Chem., <u>18</u>, N. 3, 265.
- [43] Esteso, M. A., Gonzales-Diaz, D. M., Hernandez-Luis, F. F., Fernandez-Merida, L., (1989), J. Sol. Chem., <u>18</u>, N. 3, 277.
- [44] Evans, A., (1987), "Potentiometry and Ion-selective Electrodes", John Wiley & Son, New York.
- [45] Fowler, R. H., Guggenheim, E. A., (1949), "Statistical Thermodynamics", Cambridge University Press. London.
- [46] Franks, F., (1984), "Water", Royal Society of Chemistry, London.
- [47] Freiser, H., (1978), "Ion-Selective Electrodes in Analytical Chemistry", V. 1, Plenum Press, New York.
- [48] Friedman, H. L., (1962), "Ionic Solution Theory", Interscience, New York.
- [49] Furter, W. F., (1979), "Thermodynamic Behavior of Electrolytes in Mixed Solvents", edited by Furter, W. F., Adv. Chem. Series, <u>177</u>.
- [50] Furter, W. F., (1977), Can. J. Chem. Eng., <u>55</u>, 229.
- [51] Furter, W. F., (1976), "Thermodynamic Behavior of Electrolytes in Mixed Solvents", edited by Furter, W. F., Adv. Chem. Series, <u>155</u>.

- [52] Furter, W. F., (1970), "Extractive and Azeotropic Distillation", edited by Gould, R. F., Adv. Chem. Series, <u>115</u>.
- [53] Furter, W. F., Cook, R. A., (1967), Int. J. Heat and Mass Transfer, <u>10</u>, N. 1, 23.
- [54] Gadzekpo, V. P. Y., Christian, G. D., (1984), Anal. Chem. Acta, 164, 279.
- [55] Gering, K. L., Lee L., Landis, L. H., (1989), Fluid Phase Equil., <u>48</u>, 111.
- [56] Gieskes, J. M. T. M., (1966), Z. fu Phys. Chem. Neue Folge, Bd. 50, 78.
- [57] Goldberg, R. N., (1981), J. Phys. Chem. Ref. Data., 10, N. 3, 671.
- [58] Guggenheim, E. A., Turgeon J. C., (1955), Trans. Faraday Soc., 51, 747.
- [59] Guggenheim, E.A., (1935), Phil. Mag., 19, 588.
- [60] Hàla, E., Dick, Y., Fried, V., Vilim, O., (1967), "Vapor Liquid Equilibria", Pergamon, Oxford.
- [61] Haghtalab, A., Vera, J. H., (1988), AIChE J., <u>34</u>, N. 5, 803.
- [62] Haghtalab, A., (1987), PhD Proposal, Chemical Engineering Department, McGill University, Montreal.
- [63] Hamer, W. J., Wu, Y-C, (1972), J. Phys. Chem. Ref. Data., 1, N. 4., 1047.
- [64] Harned, H. S., Robinson, R. A., (1968), "Multicomponent Electrolyte Solu tions", Pergamon, London.
- [65] Harned, H. S., Owen, B. B., (1958), "Physical Chemistry of Electrolyte Solutions", Reinhold, New York.
- [66] Harris, D. C., (1987), "Quantitative Chemical Analysis", W. H. Frieman and Compoy, New York.
- [67] Harvey, A. H., Copeman, T. W., Prausnitz, J. M., (1988), J. Phys. Chem., <u>92</u>, N. 22, 6432.

- [68] Hasa, J., Ilavsky M., Dusek, K., (1975), J. Polym Sci., Polymer Physics Edition, <u>13</u>, 253.
- [69] Hasted, J. B, Ritson, D. M., Colle C. H., (1948), J. Chem. Phys., 16, N. 1, 1.
- [70] Hiiro, K., Wakida, S-I, Yamane, M., (1988), Anal. Sci., 4, 149.
- [71] Hirschfelder, J. O., Curtis. C. F., Bird, R.B., (1964), "Molecular Theory of Gases and Liquids", John Wiley & Sons, New York.
- [72] Holmes, H. F., Baes, C. F., J.r., Mesmer, R. E., (1978), J. Chem. Thermodyn., 10, 983.
- [73] Horvath, A. L., (1985), "Handbook of Aqueous Electrolyte Solutions", Ellis Horwood Series in Physical Chemistry, Ellis Horwood Limited, John Wiley & Sons, New York.
- [74] Kakabadse, G. J., (1982), Ion-Selective Review, 3, 127.
- [75] Kawaguchi, Y., Kamar, H., Kasculara, H., Arai, Y., (1981), J. Chem. Eng. Japan, <u>14</u>, 243.
- [76] Kawaguchi, Y., Tashima, Y., Arai, Y., (1981), J. Chem. Eng. Japan, <u>14</u>, 243.
- [77] Kirkwood, J. G., Buff, F. P., (1951), J. Chem. Phys., 19, 774.
- [78] Kissel, T. R., (1986), "Physical Methods of Chemistry", "Electrochemical Methods", V. 2., edited by Rosstter, B. W., Hamitton, J. E., Wiley-Interscience Publication, New York.
- [79] Kondo, K., Eckert C. A., (1983), Ind. Eng. Chem. Fundam., 22, 283.
- [80] Koryta, J., (1975), "Ion-Selective Electrodes", Cambridge University Press, London.
- [81] Kruus, P., (1977), "Liquids and Solutions Structure Dynamics", Marcel Dekker Inc., New York.
- [82] Lebowitz, J. L., Percus, J. K., (1966), Physical Review, 144, 251.

- [83] Lanier, R. D., (1965), J. Phys. Chem., <u>69</u>, N. 11, 3992.
- [84] Lee, L. L., (1988), "Molecular Thermodynamics of Nonideal Fluids", Butterworths Series in Chemical Engineering, Boston.
- [85] Lewis, G. N., Randall M., (1961), "Thermodynamics", revised by Pitzer, K. S., Brewer, L., McGraw-Hill, New York.
- [86] Liu, Y., Harvey, A. H., Prausnitz, J. M., (1989), Chem. Eng. Comm., 77, 43.
- [87] Liu, Y., Gren, U., Wimby, M., (1989), Fluid Phase Equil., 53, 269.
- [88] Macca, C., Cakrt, M., (1983), Analy. Chim. Acta, <u>154</u>, 51.
- [89] Maurer, G., (1983), Fluid Phase Equil., <u>13</u>, 269.
- [90] McKay, H. A. C., Perring, J. K., (1953), Trans. Faraday Soc., <u>49</u>, 163.
- [91] McMillan, Jr., W. G., Mayer, J. E., (1945), J. Chem. Phys., <u>13</u>, 276.
- [92] Meissner, H. P., (1980), "Thermodynamics of Aqueous Systems with Industrial Applications", edited by Newman, S.A, ACS Symposium Series, <u>133</u>, 495.
- [93] Meissner, H. P., Kusik, C. L., (1972), AIChE J., 18, 294.
- [94] Ornstein, L. S., Zernike, F., (1914), Proc. Acad. Sci. (Amsterdam), 17, 793.
- [95] Padova, J., (1970), J. Phys. Chem., <u>74</u>, N. 26, 4587.
- [96] Panayitou, C., Vera, J. H., (1980), Fluid Phase Equil., 5. 55.
- [97] Percus, J. K., Yevick, G. J., (1958), Phys. Rev., 110, 1.
- [98] Perry, R. L., Massie, J. D., Cummings, P. T., (1988), Fluid Phase Equil., <u>39</u>, 227.
- [99] Planche, H., Renon, H., (1981), J. Phys. Chem., <u>85</u>, 3924.
- [100] Platford, R. F., (1979), "Activity Coefficients in Electrolyte Solutions", V. 1, edited by Pytkowicz, R. M., CRC Press.

- [101] Pitzer, K. S., (1980), J. Amer. Chem. Soc., <u>102</u>, N. 9, 2902.
- [102] Pitzer, K. S., (1980), "Thermodynamics of Aqueous Systems with Industrial Applications", edited by Newman, S. A., Amer. Chem. Soc. Series, Washington DC, 451.
- [103] Pitzer, K. S., (1979), "Activity Coefficients in Electrolyte Solutions", V. 1, edited by Pytkowicz, R. M., CRC Press.
- [104] Pitzer, K. S., Kim, J. J., (1974), J. Amer. Chem. Soc., <u>96</u>, N. 18, 5701.
- [105] Pitzer, K. S., (1973), J. Phys. Chem., 77, N. 2, 268.
- [106] Pitzer, K. S., Mayorga, G., (1973), J. Phys. Chem., 77, N. 19, 2300.
- [107] Pitzer, K. S., (1973), J. Phys. Chem., 77, N. 2, 268.
- [108] Powell, M. J. D., (1964), Computer J., 1, 303.
- [109] Prausnitz, J. M., Lichtenthaler, R. N., Gomes de Azevedo, E., (1986), "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice Hall Inc., Englewood Cliffs, New Jersey.
- [110] Prigogine, I., Defay, R., (1954), "Chemical Thermodynamics", Longmans, translated by Everett, D. H., London.
- [111] Pungor, E., Toth, K., Harabeczy-Pall, A., (1979), Pure & Appl. Chem., <u>51</u>, 1913.
- [112] Pytkowicz, R. M., (1983), "Equilibrium-Nonequilibrium and Natural Water", V. 1 & 2, Wiley-Interscience Publication, New York.
- [113] Pytkowicz, R. M., Johnson, K., Curtis, C., (1977), Geochem. J., 11, 1.
- [114] Renon, H., (1986), Fluid Phase Equil., <u>30</u>, 181.

* 4

- [115] Renon, H., Prausnitz, J. M., (1968), AIChE J., 14, 135.
- [116] Robinson, R. A., Stokes, R. H., (1959), "Electrolyte Solutions", Butterworths Scientific, London.

- [117] Roy, R. N., Wood, M. D., Johnson, D., Roy, L. N., (1987), J. Chem. Thermodyn., 19, 307.
- [118] Silvester, L. F., Pitzer, K. S., (1976), Lawrence Berkeley Lab, Rept. LBL-4456.
- [119] Snipes, H. P., Manly, C., Ensor, D. D., (1975), J. Chem. Eng. Data, <u>20</u>, N. 3, 287.
- [120] Skoog, D. A., (1985), "Principles of Instrumental Analysis", Saunders Colledge Pub., Philadelphia.
- [121] Sloan, J. G., (1976), "Thermodynamic Behavior of Electrolytes in Mixed Solvents", edited by Furter, W. F., Adv. Chem. Series, <u>155</u>.
- [122] Smith, J. M., Van Ness, H. C., (1975), "Introduction to Chemical Engineering Thermodynamics", McGraw-Hill, New York.
- [123] Stables, (1981), J. Phys. Chem. Ref. Data, <u>10</u>, N. 3, 779.
- [124] Stables, B. R., Nuttall, R. L., (1977), J. Phys. Chem. Ref. Data, <u>6</u>, 385.
- [125] Stokes, R. H., (1979), "Activity Coefficients in Electrolyte Solutions", V. 1, edited by Pytkowicz, R. M., CRC Press.
- [126] Stokes, R. H., Robinson, R. A., (1973), "The Physical Chemistry of Aqueous Systems", edited by Kay, R. L., Plenum Press, New York.
- [127] Stokes, R. H., Robinson, R. A., (1948), J. Amer. Chem. Soc., 70, 1870.
- [128] Usha, A. V., Raju, K., Atkinson, G., (1987), J. Phys. Chem., <u>91</u>, N. 18, 4796.
- [129] Vasheghani-Farahani, E., Vera, J. H., Cooper, D. G., Weber, M. E., (1990), Ind. Eng. Chem. Res., <u>29</u>, 554.
- [130] Vera, J. H., (1986), Fluid Phase Equil., <u>26</u>, 313.
- [131] Veselý, J., Weiss, D., Štulik, K., (1978), "Analysis with Ion-Selective Electrodes", Ellis Horwood, John Wiley & Sons, New York.
- [132] Waisman, E., Lebowitz, J. L., (1972), J. Chem. Phys., <u>56</u>, 3086.

- [133] Waisman, E., Lebowitz, J. L., (1970), J. Chem. Phys., <u>52</u>, 4307.
- [134] Wilhoit, R. C.,(1980), "Thermodynamics of Aqueous Systems with Industrial Applications", edited by Newman, S. A., ACS Series, Washington DC, 467.
- [135] Wilson, G. M., (1964), J. Amer. Chem. Soc., 86, 127.
- [136] Zemaitis, J. F., Clark, D. M., Rafal, M., Scrivner, N. C., (1986), "Handbook of Aqueous Electrolyte Thermodynamics", DIPPR, AIChE Pub., New York.

N. A
Appendix A

Method of Linear Regression and Calibration of Ion Selective Electrodes

A.1 Linear Regression

The Nernst equation is a two-parameter problem so that it can be transformed into a linear form as,

$$y = a + bx \tag{A.1}$$

where according to Nernst eq. a = E', b = S and $x = \ln a$. The slope b and intercept a are evaluated by minimization of the sum of squares of the residuals

$$F = \sum_{1}^{n} = (y_{i} - a - bx_{i}a)^{2} = \sum_{1}^{n} r_{i}^{2}$$
(A.2)

By differentiation of eq. (A.2) with respect to a and b and setting the results to zero and solving for b and a, the following equations are obtained (over all n experimental points):

$$a = \frac{\sum x^2 \sum y - \sum x \sum y}{n \sum x^2 - (\sum x)^2}$$
(A.3)

$$b = \frac{n \sum xy - \sum x \sum y}{n \sum x^2 - (\sum x)^2}$$
(A.4)

The standard deviations of the slope and of the intercept are evaluated from

$$\sigma(b) = \left\{ \frac{\sigma(y)}{n-2} \left[n \sum x^2 - (\sum x)^2 \right] \right\}^{1/2}$$
(A.5)

$$\sigma(a) = \left\{ \frac{\sigma(y) \sum x^2}{n-2} \left[n \sum x^2 - (\sum x)^2 \right] \right\}^{1/2}$$
(A.6)

where,

$$\sigma^{2}(y) = n \sum y^{2} - (\sum y)^{2} - \frac{(n \sum xy - \sum x \sum y)^{2}}{n \sum x^{2} - (\sum x)^{2}}$$
(A.7)

As a measure of linearity the correlation coefficient, R^2 , is used

$$R^{2} = \frac{\sum xy - \sum x \sum y}{\{[n \sum x^{2} - (\sum x)^{2}][n \sum y^{2} - (\sum y)^{2}]\}^{1/2}}$$
(A.8)

A.2 Calibration of Ion Selective Electrodes

In Chapter 6 the calibration of the ISE's was discussed and calibration lines, using linear regression analysis, were presented. The calibration data corresponding to the calibration lines are shown in Tables (A.1) to (A.6). The experimental electromotive force data were obtained by indicator electrodes (Na-ISE and Ca-ISE) using ion-selective electrodes as reference electrodes. The experimental mean activity coefficients of uni-univalent binary aqueous solutions were obtained from Hamer and Wu [65] and for bi-univalent binaries were those of Robinson and Stokes [116].

molality	γ_{\pm}	activity(a)	ln(a)	E(mv)	E(mv)	E(mv)	E(mv)	E(mv)
				Exp(SJE)	Exp(SJE)	Exp(SJE)	Exp	Regr
NaBr	NaBr	NaBr	NaBr	Na ⁺	Br ⁻	NaBr	NaBr	NaBr
9.000	1.949	3.08E+02	5.729	410 2	-184.7	594 9	595 7	591.8
8.000	1 649	1.74E+02	5.159	401.3	-179 2	580.5	5814	577 3
7.000	1.465	1.05E+02	4.656	393.7	-173 9	567 6	567.6	564.5
6.000	1.261	5.72E+01	4.047	383.6	-166.7	550 3	550 2	549 0
5.000	1.083	2.93E+01	3.378	373.0	-159 5	5 32 5	532 8	531 9
4.000	0.934	1.40E+01	2.636	361.3	-151.8	5131	513 2	513 0
3.000	0.816	5.99E+00	1.791	348.3	-142.2	490 5	490.6	491.5
2.500	0.768	3.69E+00	1.305	340.8	-136 7	477.5	477 6	479 1
2.000	0.730	2.13E+00	0.757	332.5	-130.6	463 1	464.1	465 2
1.800	0.717	1.67E+00	0.510	329.2	-128 0	457 2	457 0	458.9
1.500	0.709	1.13E+00	0.123	322.8	-123 3	446 1	446 0	449.1
1.200	0.669	6.44E-01	-0.439	315.7	-117.8	433.5	433 8	434.7
1.000	0.687	4.72E-01	-0.751	310 0	-114 1	424.1	424 1	426 8
0.900	0.686	3.81E-01	-0.964	307.0	-111.0	418.0	418 4	421 4
0 800	0.687	3 02E-01	-1 197	304 7	-108.1	412 8	412 8	415 4
0.600	0.692	1.72E-01	-1.758	296 4	-102.0	398.4	397 8	401 2
0.500	0 697	1.21E-01	-2.108	291.4	-97 6	389.0	389 2	392 2
0 400	0 706	7.97E-02	-2.529	285.7	-92 3	378.0	378 0	381 5
0.300	0.720	4 67E-02	-3.065	285 8	-83.7	369 5	369 6	367.9
0.200	0 742	2.20E-02	-3.816	275 2	-74 6	349 8	350 1	348 8
0.100	0 783	6.13E-03	-5.094	258.5	-58 6	317 1	317 2	316 2
0.090	0.782	4.95E-03	-5 308	255.8	-56 2	312 0	311.9	310.8
0.080	0 790	3 99E-03	-5 523	252 8	-53.5	306 3	306 4	305.3
0.070	0 798	3.12E-03	-5.770	249 5	-50 5	300 0	300.2	299 0
0.060	0.808	2.35E-03	-6 053	245.9	-46.7	292 6	292 8	291.8
0.050	0.824	1.70E-03	-6.379	241 4	-42 6	284 0	284 2	283 5
0.040	0.832	1.11E-03	-6.806	235.8	-37 3	273.1	273 5	272 6
0.030	0.849	6.49E-04	-7.341	228.9	-303	259.2	259 6	259 0
0.020	0.873	3.05E-04	-8.096	219 3	-20 5	239 8	240 0	239 8
0.010	0.903	8.15E-05	-9.414	202 9	-36	206 5	206 6	206 2
0 008	0.910	5.30E-05	-9.845	197.8	2.2	195 6	195 9	195 2
0.006	0.921	3 05E-05	-10 397	190.9	9.2	181.7	182 0	181.2
0.005	0.928	2.15E-05	-10.746	186.6	13.7	172 9	173 4	172 3

Table A.1: Electromotive force (E) measurements of Na-ISE towards single junction electrode (SJE) and Br-ISE in aqueous solutions of NaBr at 298.2 K.

molality	γ_+	activity(a)	ln(a)	E(mv)	E(mv)
				Expt	Regr
NaNO ₃					
8.000	0.378	9.14E+00	2.213	370.2	377.1
7.000	0.367	6.60E+00	1.887	366.8	369.1
6.000	0.372	4.98E+00	1.606	361.0	362.2
5.000	0.386	3.72E+00	1.315	356.7	355.0
4.000	0.408	2.66E+00	0.980	348.1	3 46.8
3.500	0.422	2.18E+00	0.780	342 .1	341.7
3.000	0.437	1.72E+00	0.542	336.4	336.0
2.500	0.456	1.30E+00	0.262	329.8	329.1
2.000	0.478	9.14E-01	-0.090	322.6	320.5
1.800	0.489	7.75E-01	-0.255	319.1	316.4
1.500	0.496	5.54E-01	-0.591	310.3	308.1
1.200	0.530	4.04E-01	-0.905	301.4	300.4
1.000	0.549	3.01E-01	-1.199	293.8	293.2
0.800	0.571	2.09E-01	-1.567	285.1	284.1
0.600	0.600	1. 30E-0 1	-2.043	272.1	272.4
0.400	0.639	6.53E-02	-2.728	254.5	255.6
0.300	0.666	3.99E-02	-3.221	242.9	243.5
0.200	0.702	1.97E-02	-3.927	225.8	226.1
0.100	0.760	5.78E-03	-5.154	196.1	195.9
0.090	0.762	4.70E-03	-5.360	191.2	190.9
0.080	0.771	3.80E-03	-5.572	185.8	185.7
0.070	0.782	3.00E-03	-5.810	180.0	179.8
0.060	0.793	2.26E-03	-6.091	173.0	172.9
0.050	0.811	1.64E-03	-6.410	164.4	165.0
0.040	0.822	1.08E-03	-6.830	155.1	154.7
0.030	0.841	6.37E-04	-7.359	141.9	141.7
0.020	0.867	3.01E-04	-8.109	122.8	123.2
0.010	0.900	8.10E-05	-9.421	90.7	91.0
0.008	0.908	5.28E-05	-9.850	80.0	80.4
0.006	0.919	3.04E-05	-10.401	66 .4	66.9
0.005	0.926	2.14E-05	-10.750	57.7	58.3

Table A.2: Electromotive Force (E) measurements of Na-ISE towards NO₃-ISE in aqueous solutions of NaNO₃ at 298.2 K.

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molality	γ_{\pm}	activity(a)	ln(a)	E(mv)	E(mv)
]			Expt	Regr
NaCl	NaCl	NaCl	NaCl	NaCl	NaCl
6.000	0.973	34.082	3.529	379.3	380.1
5.000	0.879	19.316	2.961	365.2	365.7
4.000	0.795	10.112	2.314	349.5	349.4
3.500	0.758	7.038	1.951	340.7	340.3
3.000	0.725	4.731	1.554	329.7	330.3
2.500	0.695	3.019	1.105	319.4	319.0
2.000	0.671	1.801	0.588	306.3	30 5.9
1.800	0.664	1.429	0.357	300.6	300.1
1.500	0.655	0.965	-0.035	290.5	290.2
1.200	0.650	0.608	-' .497	278.4	278.6
1.000	0.650	0.423	-0.862	269.6	269.4
0.900	0.651	0.343	-1.069	264.2	264.2
0.700	0.657	0.212	-1.553	252.2	252.0
0.500	0.670	0.112	-2.187	236.6	236.0
0.400	0.681	0.074	-2.601	226.1	225.6
0.300	0.698	0.044	-3.127	212 2	212.3
0.200	0.724	0.021	-3.835	193.0	193.7
0.100	0.771	0.006	-5.125	161.3	162.0

Table A.3: Electromotive Force (E) measurements of Na-ISE towards Cl-ISE in aqueous solutions of NaCl at 298.2 K.

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molality	γ_{\pm}	activity(a)	ln(a)	E(mv)	E(mv)
	-			Expt	Regr
CaBr ₂	CaBr ₂	CaBr ₂	$CaBr_2$	$CaBr_2$	$CaBr_2$
6.000	46.155	6.37E+07	17.970	229.6	
5.000	18.613	2.42E+06	14.699	221.2	-
4.000	7.240	7.29E+04	11.196	212.5	-
3.000	2.765	1.71E+03	7.446	202.4	—
2.000	1.125	3.42E+01	3.531	189.9	-
1.800	0.957	1.53E+01	2.730	185.9	-
1.600	0.821	6.80E+00	1.917	182.3	-
1.400	0.713	2.98E+00	1.093	177.8	-
1.200	0.627	1.28E+00	0.245	173.0	-
1.000	0.561	5.30E-01	-0.635	166.9	-
0.900	0.535	3.35E-01	-1.094	163.8	-
0.700	0.496	1.26E-01	-2.075	156.8	-
0.500	0.475	4.02E-02	-3.214	150.3	-
0.400	0.473	2.03E-02	-3.896	147.7	-
0.100	0.542	4.78E-04	-7.647	117.8	117.2
0.090	0.550	3.64E-04	-7.919	113.4	114.6
0.070	0.570	1.91E-04	-8.566	108.7	108.3
0.060	0.583	1.28E-04	-8.960	104.9	104.4
0.050	0.599	8.06E-05	-9.426	99.2	99.8
0.040	0.618	4.53E-05	-10.002	93.7	94.2
0.030	0.643	2.15E-05	-10.746	88.0	87.0
0.020	0.679	7.51E-06	-11.799	78.6	76.7
0.010	0.739	1.21E-06	-13.624	57.2	58.8

Table A.4: Electromotive force (E) measurements of Ca-ISE towards Br-ISE in aqueous solutions of CaBr₂ at 298.2 K.

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molality	γ_{\pm}	activity(a)	$\ln(\mathbf{a})$	E(mv)	E(mv)
				Expt	Regr
$Ca(NO_3)_2$	$Ca(NO_3)_2$	$Ca(NO_3)_2$	$Ca(NO_3)_2$	$Ca(NO_3)_2$	$Ca(NO_3)_2$
4.000	0.452	2.36E+01	3.163	0.4	-
3.500	0.424	1.31E+01	2.571	0.6	-
3.000	0.399	6.86E+00	1.926	0.6	-
2.500	0.375	3.30E+00	1.193	1.0	-
2.000	0.354	1.42E+00	0.350	1.0	-
1.800	0.347	9.75E-01	-0.026	1.1	-
1.400	0.336	4.16E-01	-0.876	0.6	-
1.200	0.333	2.55E-01	-1.366	0.4	-
1.000	0.331	1.45E-01	-1.931	-1.0	-
0.845	0.333	8.87E-02	-2.422	-1.6	-
0.800	0.333	7.56E-02	-2.582	-1.5	-
0.700	0.336	5.20E-02	-2.956	-0.8	-
0.600	0.341	3.43E-02	-3.374	-0.1	-
0.500	0.348	2.11E-02	-3.860	-1.0	-
0.400	0.359	1.18E-02	-4.436	-1.4	-
0.300	0.376	5.74E-03	-5.160	-3.5	-
0.200	0.407	2.16E-03	-6.139	-7.4	-
0.100	0.470	4.15E-04	-7.787	-16.9	-
0.090	0.481	3.25E-04	-8.033	-18.8	-
0.080	0.493	2.45E-04	-8.313	-20.5	-
0.070	0.507	1.79E-04	-8.629	-23.2	-
0.050	0.54 3	8.01E-05	-9.433	-30.4	-29.4
0.030	0.599	2.32E-05	10.671	-43.0	-43.5
0.020	0.644	8.55E-06	11.670	-53.8	-54.9
0.010	0.715	1.46E-06	13.436	-74.7	-75.1
0.008	0.735	8.13E-07	14.022	-82.9	-81.8

Table A.5: Electromotive force (E) measurements of Ca-ISE towards NO_3 -ISE in aqueous solutions of $Ca(NO_3)_2$ at 298.2 K.

molality	γ_{\pm}	activity(a)	ln(a)	E(mv)	E(mv)
				Expt	Regr
CaCl ₂	CaCl ₂	CaCl ₂	$CaCl_2$	CaCl ₂	CaCl ₂
6.000	11.426	1.29E+06	14.069	161.3	-
5.000	5.834	9.93E+04	11.506	144.5	-
4.000	2.910	6.31E+03	8.750	133.9	-
3.500	2.052	1.48E+03	7.301	127.2	-
3.000	1.457	3.34E+02	5.811	119.1	-
2.500	1.048	7.19E+01	4.276	109.0	-
2.000	0.773	1.48E+01	2.693	95.6	-
1.800	0.692	7.73E+00	2.045	89.5	-
1.600	0.624	3.98E+00	1.381	83.3	-
1.400	0.568	2.01E+0	0.699	75.9	-
1.200	0.023	9.89E-01	-0.011	68.5	-
1.000	0.489	4.68E-01	-0.760	59.9	60.1
0.800	0.465	2.06E-01	-1.580	49.9	49.8
0.600	0.453	8.03E-02	-2.522	38.0	3 8.0
0.500	0.452	4.62E-02	-3.075	31.1	3 1.0
0.300	0.467	1.10E-02	-4.510	13.1	13.0
0.200	0.489	3.74E-03	-5.588	-0.7	-0.6
0.100	0.539	6.26E-04	-7.376	-23.1	-23.1

Table A.6: Electromotive force (E) measurements of Ca-ISE towards Cl-ISE in aqueous solutions of $CaCl_2$ at 298.2 K.

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Appendix B

Experimental Data for the NaCl-NaNO₃-H₂O and the NaBr-NaNO₃-H₂O Systems

Electromotive force (emf) measurements for the ternary system NaCl-NaNO₃-H₂O at total ionic strengths of 1, 3 and 6 and 298.2 K are shown in Tables (B.1) to (B.3). The data were measured using a Na-ISE towards Cl-ISE as a reference electrode. Figure (B.1) shows the comparison of the results of this work with the results reported by Lanier. As the figure shows there is a little deviation at high ionic strength of NaNO₃. Similarly Tables (B.4) to (B.12) show the emf data for the NaBr-NaNO₃-H₂O system at total ionic strengths 0.3-6 and 298.2 K. The measurements were performed using a Na-ISE towards Br-ISE as a reference electrode. The experimental data regressed by the linear model explained in Appendix A. The graphical representation of the data reported in this appendix are shown in Chapter 7.

6.4

Ionic S	trength	E(mv)	activity(a)	γ_{\pm}	$\log(\gamma_{\pm})$	$\log(\gamma_{\pm})$
	U	(Expt)	(Expt)	(Expt)	(Expt)	(Regr)
NaCl	NaNO ₃	NaCl	NaCl	NaCl	NaCl	NaCl
1.000	0.000	274.5	0.432	0.657	-0.182	-0.182
0.976	0.024	273.8	0.420	0.656	-0.183	-0.183
0.931	0.069	272.4	0.398	0.654	-0.185	-0.184
0.871	0.129	270.5	0.369	0.651	-0.186	-0.186
0.818	0.182	268.6	0.343	0.648	-0.189	-0.188
0.756	0.244	266.4	0.315	0.645	-0.190	-0.190
0.704	0.296	264.3	0.290	0.642	-0.192	-0.192
0.637	0.363	261.5	0.260	0.639	-0.194	-0.195
0.5821	0.418	259.0	0.236	0.637	-0.196	-0.196
0.5291	0.471	256.3	0.213	0.634	-0.198	-0.198
0.484	0.516	253.8	0.193	0.631	-0.200	-0.200
0.447	0.553	251.6	0.177	0.629	-0 201	-0.201
0.406	0.594	249.1	0.161	0.629	-0.202	-0.203
0.373‡	0.628	246.6	0.146	0.625	 .204	-0.204
0.346	0.654	244.6	0.135	0.624	-6 202	-0.205
0.300	0.700	240.8	0.116	0.622	-0.206	-0.206
0.247‡	0.753	235.6	0.095	0.620	-0.208	-0.208
0.185‡	0.815	227.9	0.070	0.617	-0.210	-0.210
0.132‡	0.869	218.9	0.050	0.614	-0.212	-0.212
0.070±	0.930	202.6	0.026	0.611	-0.214	-0.214
0.025‡	0.975	175.2	0.009	0.606	-0.217	-0.216

Table B.1: Mean ionic activity coefficient of NaCl in aqueous solutions of NaCl and NaNO₃ at total ionic strength 1 and 298.2 K.

Ionic S	Strength	E(mv)	activity(a)	γ_{\pm}	$\log(\gamma_{\pm})$	$\log(\gamma_{\pm})$
		(Expt)	(Expt)	(Expt)	(Expt)	(Regr)
NaCl	NaNO ₃	NaCl	NaCl	NaCl	NaCl	NaCl
3.000	0.000	332.4	4.588	0.714	-0.146	-0.145
2.929	0.071	331.4	4.410	0.708	-0.150	-0.148
2.861	0.139	330.6	4.272	0.705	-0.152	- 0 .151
2.735	0.265	329.0	4.009	0.699	- 0 .155	-0.155
2.619	0.381	327.5	3.777	0.693	-0.159	-0.160
2.462	0.538	325.2	3.448	0.683	-0.165	-0.166
2.239	0.761	322.0	3.037	0.672	-0.172	-0.174
1.867	1.133	315.6	2.356	0.648	-0.188	-0.188
1.718‡	1.282	312.9	2.116	0.641	-0.193	-0.194
1.594	1.406	310.2	1.901	0.631	-0.200	-0.199
1.443‡	1.557	307.2	1.688	0.624	-0.205	-0.205
1.257‡	1.743	303.0	1.429	0.616	-0.211	-0.212
1.020‡	1.980	296.8	1.117	0.604	- 0 .219	-0.221
0.876‡	2.124	292.3	0.935	0.596	-0.224	-0.226
0.708‡	2.292	286.2	0.734	0.588	-0.231	-0.233
0.565‡	2.435	279.8	0.569	0.580	-0.237	-0.238
0.280‡	2.720	260.3	0.263	0.559	-0.253	-0.249
0.075‡	2.925	226.4	0.068	0.550	-0.260	-0.257

Table B.2: Mean ionic activity coefficient of NaCl in aqueous solutions of NaCl and NaNO₃ at total ionic strength 3 and 298.2 K.

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lonic S	trength	E(mv)	activity(a)	γ_{\pm}	$\log(\gamma_{\pm})$	$\log(\gamma_{\pm})$
	Ŭ	(Expt)	(Expt)	(Expt)	(Expt)	(Regr)
NaCl	NaNO ₃	NaCl	NaCl	NaCl	NaCl	NaCl
6.000	0.000	384.2	34.999	0.986	-0.006	-0.008
5.862	0.138	382.8	33.108	0.970	-0.013	-0.012
5.605	0.396	380.7	30.462	0.952	-0.021	-0.020
5.258	0.742	377.8	27.151	0.928	-0.033	-0.031
4.952	1.048	375.2	24.490	0.908	-0.042	-0.041
4.595	1.405	372.3	21.829	0.890	-0.051	-0.052
4.286	1.714	369.2	19.303	0.866	-0.062	-0.062
3.954‡	2.046	366.3	17.205	0.852	-0.070	-0.072
3.617	2.383	362.6	14.856	0.827	-0.082	-0.082
3.334‡	2.666	359.8	13.294	0.815	-0.089	-0.091
3.091	2.909	356.7	11.756	0.796	-0.099	-0.099
2.882‡	3.118	354.3	10.688	0.786	-0.104	-0 105
2.643	3.357	351.1	9.414	0.770	-0.113	-0.113
2.441	3.559	348.3	8. 42 4	0.758	-0.120	-0.119
2.336‡	3.664	347.0	8.001	0.755	-0.122	-0.123
2.227‡	3.773	345.3	7.479	0.748	-0.126	-0.126
2.082‡	3.918	343.0	6.827	0.739	-0.131	-0.131
1.790‡	4.210	338.1	5.621	0.723	-0.141	-0.140
1.460‡	4.540	331.8	4. 37 8	0.707	-0.151	-0.150
1.052‡	4.948	322.0	2.968	0.686	-0.164	-0.163
0.704	5.296	310.8	1.903	0.671	-0.173	-0.174
0.443‡	5 557	298.1	1.150	0.658	-0.182	-0.182

Table B.3: Mean ionic activity coefficient of NaCl in aqueous solutions of NaCl and NaNO₃ at total ionic strength 6 and 298.2 K.

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Figure (B.1): Comparison of mean activity coefficient of NaCl in aqueous solution of NaCl and NaNO3 with the results reported by Lanier at various ionic strengths and 298.2 K.

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Ionic S	Strength	E(mv)	activity(a)	γ_{\pm}	$\ln(\gamma_{\pm})$	$\ln(\gamma_{\pm})$
	_	(Expt)	(Expt)	(Expt)	(Expt)	(Regr)
NaBr	NaNO ₃	NaBr	NaBr	NaBr	NaBr	NaBr
0.300	0.000	368.8	4.68E-02	0.721	-0.327	-0.326
0.286	0.014	367.5	4.45E-02	0.721	-0.328	-0.329
0.273	0.027	366.2	4.23E-02	0.719	-0.330	-0.331
0.261	0.039	364.9	4.02E-02	0.717	-0.333	-0.333
0.245	0.055	363.2	3.76E-02	0.715	-0.335	-0.335
0.231	0.069	361.5	3.52E-02	0.713	-0.339	-0.338
0.214	0.086	359.5	3.25E-02	0.711	-0.341	-0.341
0.200	0.100	357.6	3.02E-02	0.709	-0.344	-0.343
0.182	0.118	355.1	2.74E-02	0.708	-0.346	-0.346
0.167‡	0.133	352.8	2.50E-02	0.707	-0.347	-0.348
0.159	0.141	351.4	2.37E-02	0.704	-0.351	-0.350
0.154‡	0.146	350.6	2.29E-02	0.704	-0.351	-0.351
0.140‡	0.160	348.1	2.08E-02	0.703	-0.352	-0.353
0.131	0.169	346.2	1.93E-02	0.702	-0.354	-0.354
0.126	0.174	345.3	1.86E-02	0.701	-0.355	-0.355
0.120	0.180	344.0	1.77E-02	0.700	-0.356	-0.356
0.111‡	0.189	342.0	1.64E-02	0.700	-0.357	-0.358
0.110	0.190	341.6	1.61E-02	0.699	-0.357	-0.358
0.102	0.198	339.6	1.49E-02	0.698	-0.360	-0.359
0.097‡	0.203	338.3	1.41E-02	0.698	-0.360	-0.360
0.082	0.218	333.9	1.19E-02	0.696	-0.363	-0.363
0.069‡	0.231	329.6	1.00E- 0 2	0.695	-0.364	-0.365
0.055	0.245	323.6	7.94E-03	0.692	-0.368	-0.367
0.039‡	0.261	314.8	5.62E-03	0.691	-0.369	-0.370
0.027‡	0.273	305.5	3.90E-03	0.690	-0.372	-0.372
0.014‡	0.286	288.9	2.03E-03	0.688	-0.374	-0.374

Table B.4: Mean ionic activity coefficient of NaBr in aqueous solutions of NaBr and NaNO₃ at total ionic strength 0.3 and 298.2 K.

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Ionic S	Strength	E(mv)	activity(a)	γ_{\pm}	$\ln(\gamma_{\pm})$	$\ln(\gamma_{\pm})$
	_	(Expt)	(Expt)	(Expt)	(Expt)	(Regr)
NaBr	NaNO ₃	NaBr	NaBr	NaBr	NaBr	NaBr
0.500	0.000	394.0	0.121	0.697	-J.361	-0.356
0.476	0.024	392.4	0.114	0.692	-0.368	-0.360
0.455	0.045	391.1	0.108	0.690	-0.370	-0.363
0.426	0.074	389.3	0.101	0.689	-0.373	-0.368
0.400	0.100	387.4	0.094	0.684	-0.379	-0.372
0.371	0.129	385.3	0.086	0.682	-0.382	-0.376
0.345	0.155	383.3	0.080	0.680	-0.386	-0.381
0.313	0.187	380.5	0.071	0.676	-0.391	-0.386
0.286‡	0.214	378.0	0.065	0.673	-0.396	-0.390
0.263	0.237	375.6	0.059	0.669	-0.402	-0.393
0.244	0.256	373.5	0.054	0.667	-0.405	-0.396
0.228‡	0.272	371.7	0.051	0.667	-0.405	-0.399
0.209‡	0.291	369.3	0.046	0.664	-0.409	-0.402
0.193	0.307	367.0	0.042	0.661	-0.414	-0.405
0.179‡	0.321	365.2	0.039	0.662	-0.412	-0.407
0.172‡	0.328	364.1	0.038	0.660	-0.415	-0.408
0.149‡	0.351	360.3	0.032	0.658	-0.419	-0.411
0.123‡	0.377	355.1	0.026	0.655	-0.423	-0.416
0.100‡	0.400	349.6	0.021	6.651	-0.429	-0.419
0.075‡	0.425	342.0	0.016	0.650	-0.431	-0 423
0.046‡	0.454	329.2	0.010	0.647	-0.435	-0.428
0.024‡	0.476	312.4	0.005	0.643	-0.442	-0.431

Table B.5: Mean ionic activity coefficient of NaBr in aqueous solutions of NaBr and NaNO₃ at total ionic strength 0.5 and 298.2 K.

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Ionic S	Strength	E(mv)	activity(a)	γ_{\pm}	$\ln(\gamma_{\pm})$	$\ln(\gamma_{\pm})$
	Ū	(Expt)	(Expt)	(Expt)	(Expt)	(Regr)
NaBr	NaNO ₃	NaBr	NaBr	NaBr	NaBr	NaBr
1.000	0.000	428.9	0.472	0.687	-0.375	-0.377
0.953	0.047	427.3	0.443	0.682	-0.383	-0.381
0.909	0.091	426.0	0.421	0.681	-0.385	-0.385
0.852	0.148	424.0	0.389	0.676	-0.391	-0.390
0.801	0.199	422.2	0.363	0.673	-0.396	-0.395
0.742	0.258	420.0	0.333	0.670	-0.401	-0.400
0.691	0.309	417.9	0.306	0.666	-0.406	-0.405
0.646	0.354	416.1	0.286	0.665	-0.408	-0.409
0.589	0.411	413.4	0.257	0.660	-0.415	-0.414
0.542	0.458	411.1	0.235	0.658	-0.418	-0.418
0.501	0.499	409.0	0.216	0.657	-0.421	-0.422
0.466	0.534	407.0	0.200	0.654	-0.424	-0.425
0.427‡	0.573	404.6	0.182	0.653	-0 427	-0.429
0.393	0.607	402.3	0.166	0.650	-0.431	-0.432
0.356	0.644	399.6	0.149	0.648	-0.434	-0.435
0.329‡	0.671	397.6	0.138	0.648	-0.434	-0.437
0.311‡	0.689	396.0	0.130	0.645	-0.438	-0.439
0.260‡	0.740	391.1	0.107	0.641	-0.444	-0.443
0.201‡	0.799	384.3	0.082	0.639	-0.448	-0.449
0.150‡	0.850	376.5	0.060	0.635	-0.454	-0.453
0.091‡	0.909	363.6	0.036	0.631	-0.461	-0.459
0.048‡	0.952	347.0	0.019	0.629	-0.464	-0.463

Table B.6: Mean ionic activity coefficient of NaBr in aqueous solutions of NaBr and NaNO₃ at total ionic strength 1 and 298.2 K.

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Ionic S	trength	E(mv)	activity(a)	γ_{\pm}	$\ln(\gamma_{\pm})$	$\ln(\gamma_{\pm})$
		(Expt)	(Expt)	(Expt)	(Expt)	(Regr)
NaBr	$NaNO_3$	NaBr	NaBr	NaBr	NaBr	NaBr
2.000	0.000	469.3	2.132	0.730	-0.315	-0.317
1.906	0.094	467.6	1.994	0.723	-0.324	-0.328
1.820	0.180	465 .8	1.858	0.714	-0.336	-0.338
1.741	0.259	464.2	1.745	0.708	-0.346	-0.347
1.636	0.364	46 1.8	1.588	0.697	-0.361	-0.360
1.513	0.487	459.1	1.428	0.687	-0.375	-0.374
1.408	0.592	456.6	1.295	0.678	-0.388	-0.387
1.316	0.684	454.3	1.183	0.670	-0.400	-0.397
1.303	0.697	454.0	1.169	0.670	-0.401	-0.399
1.235	0.765	452.3	1.093	0.665	-0.408	-0.407
1.199	0.801	451.3	1.051	0.662	-0.412	-0.411
1.171	0.829	450.5	1.019	0.659	-0.416	-0.414
1.101	0.899	448.5	0.942	0.654	-0.425	-0.423
1.096‡	0.904	448.3	0.934	0.653	-0.426	-0.423
1.017	0.983	446.0	0.854	0.648	-0.434	-0.433
0.9 93 ‡	1.007	445.3	0.831	0.647	-0.436	-0.436
0.938‡	1.062	443.6	0.777	0.643	-0.441	-0.442
0.884	1.116	441.5	0.715	0.636	-0.452	-0.448
0.845‡	1.155	440.4	0.685	0.637	-0.452	-0.453
0.797	1.203	438.3	0.631	0.629	-0.463	-0.459
0.735‡	1. 26 5	436.2	0.581	0.629	-0.464	-0.466
0.648‡	1.352	432.7	0.506	0.625	-0.470	-0.476
0.549‡	1.451	427.7	0.416	0.615	-0.485	-0.488
0.465‡	1.535	423.1	0.347	0.611	-0.492	-0.498
0.370‡	1.630	416.6	0.269	0.603	-0.506	-0.509
0.263‡	1.737	407.2	0.186	0.595	-0.520	-0.522
0.183‡	1.817	397.4	0.127	0.587	-0.532	-0.531
0.096‡	1.904	380.2	0.064	0.579	-0.547	-0.541

Table B.7: Mean ionic activity coefficient of NaBr in aqueous solutions of NaBr and NaNO₃ at total ionic strength 2 and 298.2 K.

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Ionic S	trength	E(mv)	activity(a)	γ_{\pm}	$\ln(\gamma_{\pm})$	$\ln(\gamma_{\pm})$
	Ũ	(Expt)	(Expt)	(Expt)	(Expt)	(Regr)
NaBr	NaNO ₃	NaBr	NaBr	NaBr	NaBr	NaBr
3.000	0.000	494.8	5.993	0.816	-0.203	-0.199
2.859	0.141	493.1	5.606	0.808	-0.213	-0.216
2.731	0.269	491.0	5.162	0.794	-0.231	-0.233
2.559	0.441	488.1	4.606	0.775	-0.255	-0.254
2.407	0.593	485.5	4.159	0.759	-0.276	-0.274
2.231	0.769	482.4	3.683	0.742	-0.299	-0.296
2.078	0.922	480.0	3.351	0.733	-0.310	-0.315
1.945	1.055	477.3	3.014	0.719	-0.330	-0.332
1.775	1.225	473.8	2.627	0.702	-0.353	-0.354
1.734	1.266	472.7	2.516	0.695	-0.363	-0.359
1.632	1.368	470.8	2.335	0.691	-0.370	-0.372
1.615‡	1.385	470.1	2.272	0.685	-0.379	-0.374
1.511	1.489	468.2	2.108	0.682	-0.383	-0.387
1.406	1.594	465.6	1.904	0.672	-0.398	-0.400
1.389‡	1.611	465.2	1.874	0.671	-0.400	-0.402
1.315	1.685	463.2	1.733	0.663	-0.411	-0.412
1.261‡	1.739	461.9	1.646	0.660	-0.416	-0.419
1.246	1.754	461.3	1.608	0.656	-0.422	-0.421
1.075‡	1.925	456.5	1.332	0.643	-0.442	-0.442
0.940	2.060	452.0	1.116	0.629	-0.464	-0.459
0.786‡	2.214	446.5	0.899	0.617	-0.482	-0.479
0.6071	2.393	439.0	0.670	0.607	-0.500	-0.501
0.4521	2.548	430.5	0.480	0.595	-0.520	-0.521
0.276‡	2.724	416.8	0.280	0.581	-0.543	-0.543
0.145	2.855	399.4	0.141	0.571	-0.561	-0.560

Table B.8: Mean ionic activity coefficient of NaBr in aqueous solutions of NaBr and NaNO₃ at total ionic strength 3 and 298.2 K.

Ionic S	Strength	E(mv)	activity(a)	γ_{\pm}	$\ln(\gamma_{\pm})$	$\ln(\gamma_{\pm})$
		(Expt)	(Expt)	(Expt)	(Expt)	(Regr)
NaBr	NaNO ₃	NaBr	NaBr	NaBr	NaBr	NaBr
4.000	0.000	517.5	13.958	0.934	-0.068	-0.071
3.813	0.187	515.2	12.752	0.914	-0.089	-0.095
3.643	0.357	512.7	11.560	0.891	-0.116	-0.117
3.487	0.513	510.6	10.645	0.874	-0.135	-0.136
3.277	0.723	507.6	9.462	0.850	-0.163	-0.163
3.091	0.909	505.0	8.543	0.831	-0.185	-0.187
2.873	1.127	501.6	7.476	0.807	-0.215	-0.214
2.684	1.316	498.7	6.671	0.788	-0.238	-0.238
2.443	1.557	494.4	5.634	0.759	-0.275	-0.269
2.241	1.759	491.1	4.950	0.743	-0.297	-0.294
2.071	1.929	488.1	4.400	0 .729	-0.316	-0.316
2.019‡	1.981	486.8	4.181	0 .719	-0.329	-0.322
1.924	2.076	485.2	3.926	0.714	-0.337	-0.334
1.797‡	2.203	482.6	3.545	0.702	-0.353	-0.351
1.758‡	2.242	481.8	3.435	0.699	-0.358	-0.355
1.594	2.406	478.3	2.994	0.685	-0 378	-0.376
1.587‡	2.413	478.4	3.006	0.688	-0.374	-0.377
1.350‡	2.650	472.5	2.384	0.664	-0.409	-0.407
1.159‡	2.841	467.6	1.967	0.651	-0.429	-0.431
0.937‡	3.063	460.6	1.494	0.631	-0.460	-0.460
0.746‡	3.254	453.6	1.135	0.617	-0.483	-0.484
0.531‡	3.469	443.6	0.766	0.601	-0.509	-0.511
0.370‡	3.630	433.5	0.516	0.590	-0.527	-0.531
0.194‡	3.806	415.9	0.258	0.577	-0.550	-0.554

Table B.9: Mean ionic activity coefficient of NaBr in aqueous solutions of NaBr and NaNO₃ at total ionic strength 4 and 298.2 K.

Ionic S	Strength	E(mv)	activity(a)	γ_{\pm}	$\ln(\gamma_{\pm})$	$\ln(\gamma_{\pm})$
	Ũ	(Expt)	(Expt)	(Expt)	(Expt)	(Regr)
NaBr	NaNO ₃	NaBr	NaBr	NaBr	NaBr	NaBr
5.000	0.000	535.5	29.322	1.083	0.080	0.080
4.767	0.233	532.5	25.93 8	1.043	0.042	0.052
4.555	0.445	530.2	23.611	1.018	0.018	0.026
4.361	0.639	528.1	21.669	0.997	-0.003	0.002
4.100	0.900	525.1	19.168	0.967	-0.034	-0.029
3.796	1.204	521.5	16.545	0.934	-0.069	-0.066
3.534	1.466	518.3	14.517	0.906	-0.098	-0.098
3.253	1.747	514.7	12.530	0.878	-0.131	-0.133
2.970	2.030	510.8	10.684	0.848	-0.165	-0.167
2.733	2.267	507.4	9.298	0.825	-0.192	-0.196
2.530	2.470	504.4	8.225	0.806	-0.215	-0.221
2.329‡	2.671	501.2	7.216	0.787	-0.239	-0.245
2.157	2.843	498.3	6.410	0.771	-0.260	-0.266
2.088‡	2.912	497.1	6.103	0.765	-0.269	-0.274
2.029	2.971	496.1	5.858	0.760	-0.275	-0.282
1.903‡	3.097	493.8	5.333	0.749	-0.290	-0.297
1.694‡	3.306	489.7	4.510	0.730	-0.315	-0.323
1.517‡	3.483	485.9	3.861	0.714	-0.338	-0.344
1.320‡	3.680	481.3	3.199	0.696	-0.362	-0.368
1.099‡	3.901	475.5	2.524	0.678	- 0.3 89	-0.395
0.850‡	4.150	467.6	1.828	0.656	-0.422	-0.425
0.666‡	4.334	460.4	1.362	0.639	-0.447	-0.448
0.465	4.535	450.1	0.894	0.620	-0.478	-0.472
0.244	4.756	432.8	0.441	0.601	-0.508	-0.499
0.125‡	4.875	416.0	0.222	0.596	-0.518	-0.514

Table B.10: Mean ionic activity coefficient of NaBr in aqueous solutions of NaBr and NaNO₃ at total ionic strength 5 and 298.2 K.

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Ionic S	trength	E(mv)	activity(a)	γ_{\pm}	$\ln(\gamma_{\pm})$	$\ln(\gamma_{\pm})$
		(Expt)	(Expt)	(Expt)	(Expt)	(Regr)
NaBr	NaNO ₃	NaBr	NaBr	NaBr	NaBr	NaBr
6.000	0.000	553.1	57.244	1.261	0.232	0.228
5.722	0.278	550.4	51.486	1.225	0.203	0.194
5.469	0.531	547.5	45.944	1.183	0.168	0.163
5.237	0.763	544.9	41.484	1.149	0.139	0.134
4.924	1.076	541.2	35.874	1.102	0.097	0.095
4.646	1.354	537.9	31.514	1.063	0.061	0.061
4.321	1.679	533.9	26.933	1.019	0.019	0.021
4.039	1.961	530.2	23.291	0.980	-0 020	-0.014
3.791	2.209	526.9	20.460	0.948	-0.053	-0.045
3.471	2.529	522.6	17.281	0.911	-0.093	-0.084
3.201	2.799	519.0	15.003	0.884	-0.124	-0.117
2.970‡	3.030	515.7	13.179	0.860	-0.151	-0.146
2.740	3.260	512.2	11.487	0.836	-0.179	-0.175
2.542‡	3.458	509.4	10.291	0 821	-0.197	-0.199
2.513	3.487	508.7	10.012	0.815	-0.205	-0.203
2.395‡	3.605	506.7	9.256	0.803	-0.220	-0.217
2.169‡	3.831	502.9	7.972	0.783	-0.245	-0.245
1.900‡	4.100	497.9	6.551	0.758	-0.277	-0.278
1.589‡	4.411	491.6	5.115	0.732	-0.311	-0.317
1.228‡	4.772	482.2	3.536	0.693	-0.367	-0.361
0.916‡	5.084	473.1	2.474	0.671	-0.399	-0.400
0.560‡	5.440	458.5	1.394	0.644	-0.440	-0.444
0.294‡	5.706	440.5	0.688	0.625	-0.471	-0.477
0.151‡	5.849	422.6	0 340	0.614	-0.488	-0.494

Table B.11: Mean ionic activity coefficient of NaBr in aqueous solutions of NaBr and NaNO₃ at total ionic strength 6 and 298.2 K.

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Appendix C

Experimental Data for the $NaBr-Ca(NO_3)_2-H_2O$ System

Experimental data for the NaBr-Ca(NO₃)₂-H₂O system are shown in Tables (C.1) to (C.3). As explained in Chapter 7, the electromotive force of the Na-ISE towards Br-ISE as a reference electrode were measured. The values were linearly regressed as explained in Appendix A. To show the consistency and precision of the data, the potential of the Na-ISE towards a single junction and a double junction electrode was also measured. Tables (C.4) to (C.6) show the potential of the Na-ISE and the Br-ISE with reference to the two junction electrodes. As explained in Chapter 7, E(NaBr) is the difference in the potentials of the Na-ISE and the reference electrode. It can be seen that the three values of E(NaBr) are very close. However in the calculation of the mean activity coefficient of NaBr we always use the data obtained by Br-ISE as a reference electrode because it eliminates liquid junction potentials.

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Ionic	Strength	E(mv)	activity(a)	γ_{\pm}	$\ln(\gamma_{\pm})$	$\ln(\gamma_{\pm})$
		(Expt)	(Expt)	(Expt)	(Expt)	(Regr)
NaBr	$Ca(NO_3)_2$	NaBr	NaBr	NaBr	NaBr	NaBr
3.000	0.000	493.9	5.993	0.816	-0.203	-0.199
2.853	0.147	490.6	5.264	0.804	-0.218	-0.213
2.720	0.280	487.7	4.698	0.797	-0.227	-0.225
2.598	0.402	484.8	4.192	0.788	-0.238	-0.236
2.435	0.565	480.8	3.583	0.777	-0.252	-0.250
2.291	0.709	477.1	3.098	0.768	-0.264	-0.263
2.124	0.876	472.5	2.586	0.757	-0.278	-0.279
1.980	1.020	468.3	2.193	0.748	-0.290	-0.292
1.854	1.146	464.4	1.882	0.740	-0.301	-0.303
1.692	1.308	459.1	1.528	0.731	-0.314	-0.318
1.556‡	1.444	454.3	1.265	0.723	-0.325	-0.330
1.441‡	1.559	449.8	1.061	0.715	-0.336	-0.340
1.311	1.689	444.5	0.861	0.708	-0.345	-0.352
1.203	1.797	439.6	0.710	0.701	-0.355	-0.362
1.044‡	1.956	431.3	0.513	0.686	-0.377	-0.376
0.912‡	2.088	423.9	0.384	0.679	-0.387	-0.388
0.760‡	2.240	413.9	0.259	0.669	-0.402	-0.402
0.632‡	2.368	403.9	0.175	0.662	-0.413	-0.413
0.487‡	2.513	390.0	0.101	0.653	-0.426	-0.426
0.381‡	2.619	377.0	0.061	0.647	-0.435	-0.436
0.265‡	2.735	357.8	0.029	0.638	-0.450	-0.447
0.139‡	2.861	323.7	0.007	0.624	-0.472	-0.458

Table C.1: Mean ionic activity coefficient of NaBr in aqueous solutions of NaBr and $Ca(NO_3)_2$ at total ionic strength 3 and 298.2 K.

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lonic	Strength	E(mv)	activity(a)	γ_{\pm}	$\ln(\gamma_{\pm})$	$\ln(\gamma_{\pm})$
		(Expt)	(Expt)	(Expt)	(Expt)	(Regr)
NaBr	$Ca(NO_3)_2$	NaBr	NaBr	NaBr	NaBr	NaBr
4.500	0.000	525.7	20.453	1.005	0.005	0.010
4.386	0.114	523.9	19.057	0.995	-0.005	-0.001
4.174	0.326	520.6	16.741	0.980	-0.020	-0.021
3.891	0.609	515.5	13.703	0.951	-0.050	-0.048
3.645	0.855	511.2	11.574	0.933	-0.069	-0.071
3.361	1.139	505.6	9.289	0.907	-0.098	-0.098
3.118	1.382	500.8	7.693	0.889	-0.117	-0.121
2.860	1.640	495.0	6.126	0.865	-0.145	-0.146
2.641	1.859	489.9	5.014	0.848	-0.165	-0.167
2.419	2.081	484.5	4.056	0.833	-0.183	-0.188
2.232‡	2.268	479.5	3.333	0.818	-0.201	-0.206
2.071‡	2.429	474.9	2.782	0.805	-0.216	-0.221
1.911	2.589	469.7	2.268	0.788	-0.238	-0.236
1.755	2.745	464.6	1.857	0.776	-0.253	-0.251
1.623	2.877	459.9	1.544	0.765	-0.267	-0.263
1.510‡	2.990	456.0	1.325	0.762	-0.271	-0.274
1.408	3.092	451.8	1.123	0.752	-0.284	-0.284
1.190‡	3.310	442.1	0.767	0.736	-0.307	-0.305
1.006‡	3.494	432.7	0.530	0.724	-0.322	-0.322
0.799‡	3.701	420.0	0.322	0.711	-0.342	-0.342
0.566‡	3.934	401.4	0.155	0.696	-0.362	-0.364
0.394‡	4.106	382.0	0.072	0.683	-0.381	-0.380
0.206‡	4.294	348.0	0.019	0.670	-0.400	-0.398
0.105‡	4.395	313.3	0.005	0.663	-0.411	-0.408

Table C.2: Mean ionic activity coefficient of NaBr in aqueous solutions of NaBr and $Ca(NO_3)_2$ at total ionic strength 4.5 and 298.2 K.

Ionic	Strength	E(mv)	activity(a)	γ_{\pm}	$\ln(\gamma_{\pm})$	$\ln(\gamma_{\pm})$
		(Expt)	(Expt)	(Expt)	(Expt)	(Regr)
NaBr	$Ca(NO_3)_2$	NaBr	NaBr	NaBr	NaBr	NaBr
6.000	0.000	554.0	57.244	1.261	0.232	0.233
5.846	0.154	552.0	52.920	1.244	0.219	0.216
5.560	0.440	547.7	44.698	1.203	0.184	0.186
5.300	0.700	543.8	38.351	1.168	0.156	0.158
4.954	1.046	538.3	30.901	1.122	0.115	0.121
4.650	1.350	533.4	25.492	1.086	0.082	0.088
4.298	1.702	527.6	20.300	1.048	0.047	0.051
3.927	2.073	521.1	15.727	1.010	0.010	0.011
3.615	2.385	515.3	12.523	0.979	-0.021	-0.023
3.348	2.652	509.9	10.130	0.951	-0.051	-0.051
3.076	2.924	504.2	8.099	0.925	-0.078	-0.080
2.845	3.155	499.2	6.655	0.907	-0.098	-0.105
2.647‡	3.353	494.4	5.512	0.887	-0.120	-0.127
2.421‡	3.579	488.7	4.406	0.867	-0.143	-0.151
2.286‡	3.714	484.7	3.766	0.849	-0.164	-0.165
2.276	3 .724	484.6	3.751	0.851	-0.161	-0.166
2.107‡	3.893	479.9	3.119	0.838	-0.176	-0.184
1.993‡	4.007	475.9	2.665	0.819	-0.199	-0.197
1.722‡	4.278	466.8	1.865	0.793	-0.232	-0.226
1.412‡	4.588	455.3	1.187	0.772	-0.259	-0.259
1.149‡	4.851	443.3	0.741	0.749	-0.289	-0.287
0.853‡	5.147	426.5	0.383	0.726	-0.321	-0.319
0.635‡	5.365	410.6	0.205	0.713	-0.338	-0.342
0.398‡	5.602	385.6	0.077	0.697	-0.361	-0.368
0.139‡	5.861	329.2	0.008	0.660	-0.415	-0.395

Table C.3: Mean ionic activity coefficient of NaBr in aqueous solutions of NaBr and $Ca(NO_3)_2$ at total ionic strength 6 and 298.2 K.

[†] Data obtained using NaBr as a titrant

Ionie	c Strength	E(I	Na ⁺)	E(1	3r ⁻)	T	E(NaF	Br)
) (n	nv)	(n	nv)		(mv))
NaBr	$Ca(NO_3)_2$	SJE★	DJE†	SJE	DJE	SJE	DJE	Br-ISE‡
3.000	0.000	352.8	326.2	-141.0	-167.6	493.8	493.8	493.9
2.853	0.147	351.4	324.3	-139.4	-166.3	490.8	490.6	490.6
2.720	0.280	349.4	322.4	-137.9	-165.1	487.3	487.5	487.7
2.598	0.402	348.2	320.7	-136.4	-163.9	484.6	484.6	484.8
2.435	0.565	346.2	318.5	-134.4	-162.1	480.6	480.6	480.8
2.291	0.709	344.4	316.4	-132.5	-160.5	476.9	476.9	477.1
2.124	0.876	342.1	313.9	-130.2	-158.4	472.3	472.3	472.5
1.980	1.020	340.0	311.6	-128.0	-156.4	468.0	468.0	468.3
1.854	1.146	338.2	309.6	-126.1	-154.6	464.3	464.2	464.4
1.692	1.308	335.7	30 6.8	-123.2	-152.1	458.9	458.9	459.1
1.556	1.444	333.3	304.3	-120.8	-149.8	454.1	454.1	454.3
1.441	1.559	331.1	302.1	-118.6	-147.4	449.7	449.5	449.8
1.311	1.689	328.5	299.2	-115.7	-145.1	444.2	444.3	444.5
1.203	1.797	326.2	296. 8	-113.2	-142.6	439.4	439.4	439.6
1.044	1.956	322.1	291.2	-109.0	-140.0	431.1	431.2	431.3
0.912	2.088	318.4	287.6	-105.2	-136.1	423.6	423.7	423.9
0.760	2.240	313.6	282.9	-100.1	-130.8	413.7	413.7	413.9
0.632	2.368	308.7	278.2	-95.0	-125.4	403.7	403.6	403.9
0.487	2.513	301.9	271.8	-87.8	-118.0	389.7	389.8	390.0
0.381	2.619	295.7	265.9	-81.1	-110.8	376.8	376.7	377.0
0.265	2.735	286.2	256.9	-71.3	-100.7	357.5	357.6	357.8
0.139	2.861	269.5	240.1	-54.1	-83.2	323.6	323.3	323.7

Table C.4: Experimental electromotive force of Na-ISE towards single junction electrode, double junction electrode and Br-ISE in aqueous solution of NaBr and $Ca(NO_3)_2$ at total ionic strength 3 and 298.2 K.

* reference: Single Junction Electrode

† reference: Double Junction Electrode

‡ reference: Bromide Ion-Selective Electrode

N.

Ionic	: Strength	E(N	la ⁺)	E(E	Br ⁻)		E(NaB	lr)
		(n	nv)	(п	ıv)		(mv)	
NaBr	$Ca(NO_3)_2$	SJE★	DJE†	SJE	DJE	SJE	DJE	Br-ISE‡
4.500	0.000	373.6	343.5	-151.5	-181.7	525.1	525.2	525.7
4.386	0.114	372.6	342.4	-151.0	-181.2	523.6	523.6	523.9
4.174	0.326	370.7	340.5	-149.6	-179.8	520.3	520.3	520.6
3.891	0.609	368.0	337.4	-147.5	-178.2	515.5	515.6	515.5
3.645	0.855	365.6	334.8	-145.6	-176.3	511.2	511.1	511.2
3.361	1.139	362.6	331.7	-143.0	-173.8	505.6	505.5	505.6
3.118	1.382	360.1	328.8	-140.6	-171.7	500.7	500.5	500.8
2.860	1.640	357.2	325.8	-137.7	-169.1	494.9	494.9	49.5.0
2.641	1.859	354.5	322.9	-135.4	-167.0	489.9	489.9	489.9
2.419	2.081	351.6	319.9	-132.9	-164.5	484.5	484.4	484.5
2.232	2.268	349.1	317.6	-130.5	-161.9	479.6	479.5	479.5
2.071	2.429	346.8	315.2	-128.4	-159.8	475.2	475.0	474.9
1.911	2.589	344.1	305.6	-125.6	-164.0	469.7	469.6	469.7
1.755	2.745	341.6	302.6	-122.9	-161.9	464.5	464.5	464.6
1.623	2.877	339.4	300.2	-120.8	-159.9	460.2	460.1	459.9
1.510	2.990	337.3	298.8	-118.5	-156.9	455.8	455.7	456.0
1.408	3.092	335.5	299.9	-115.9	-151.6	451.4	451.5	451.8
1.190	3.310	330.7	294.7	-110.7	-147.0	441.4	441.7	442.1
1.006	3.494	326.1	289.7	-106.0	-142.6	432.1	432.3	432.7
0.799	3.701	319.9	283.0	-99.5	-136.5	419.4	419.5	420.0
0.566	3.934	310.7	273.4	-90.5	-127.9	401.2	401.3	401.4
0.394	4.106	301.2	263.4	-80.6	-118.6	381.8	382.0	382.0
0.206	4.294	284.1	244.7	-62.6	-102.1	346.7	346.8	348.0
0.105	4.395	267.0	227.3	-46 6	-86.0	313.6	313.3	313.3

Table C.5: Experimental electromotive force of Na-ISE towards single junction electrode, double junction electrode and Br-ISE in aqueous solution of NaBr and $Ca(NO_3)_2$ at total ionic strength 4.5 and 298.2 K.

* reference: Single Junction Electrode

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† reference: Double Junction Electrode

‡ reference: Bromide Ion-Selective Electrode

Ionic	Strength	E(N	la ⁺)	E(B	lr ⁻)	E(NaBr)		Br)
	0	(п	nv)	(m	iv)		(mv)	
NaBr	$Ca(NO_3)_2$	SJE*	DJE†	SJE	DJE	SJE	DJE	Br-ISE‡
6.000	0.000	389.2	367.1	-164.8	-186.8	554.0	553.9	554.0
5.846	0.154	388.0	366.7	-163.7	-185.1	551.7	551.8	552.0
5.560	0.440	385.8	364.1	-161.8	-183.4	547.6	547.5	547.7
5.300	0.700	383.7	361.6	-160.0	-182.0	543.7	543.6	543.8
4.954	1.046	380.8	358.5	-157.5	-179.8	53 8. 3	538.3	538.3
4.650	1.350	378.1	355.4	-155.2	-178.0	533.3	533.4	533.4
4.298	1.702	374.9	351.9	-152.5	-175.6	527.4	527.5	527.6
3.927	2.073	371.4	348.2	-149.6	-172.7	521.0	520.9	521.1
3.615	2.385	368.3	344.6	-146.7	-170.3	515.0	514.9	515.3
3.348	2.652	365.4	341.6	-144.3	-168.1	509.7	509.7	509.9
3.076	2.924	362.5	338.4	-141.3	-165.6	503.8	504.0	504.2
2.845	3.155	359.7	335.8	-139.2	-163.1	498.9	498.9	499.2
2.647	3.353	357.3	333.3	-137.0	-161.3	494.3	494.6	494.4
2.421	3.579	354.4	330.3	-134.1	-158.2	488.5	488.5	488.7
2.286	3.714	352.8	327.3	-132.0	-156.1	484.8	483.4	484.6
2.107	3.893	350.1	325.5	-129.6	-154.3	479.7	479.8	479.9
1.993	4.007	348.3	322.9	-127.3	-152.9	475.6	475.8	475.9
1.722	4.278	344.2	318.4	-122.4	-148.4	466.6	466.8	466.8
1.412	4.588	338.4	312.5	-116.6	-142.3	455.0	454.8	455.3
1.149	4.851	332.4	306.6	-111.0	-136.6	443.4	443.2	443.3
0.853	5.147	324.2	298.4	-101.9	-127.9	426.1	426.3	426.5
0.635	5. 36 5	316.2	290 .5	-94.1	-119.9	410.3	410.4	410.6
0.398	5.602	303.8	278.2	-81.7	-107.3	385.5	385.5	3 85.6
0.139	5.861	275.8	250.3	-53.3	-78.7	329.1	328.7	329.2

Table C.6: Experimental electromotive force of Na-ISE towards single junction electrode, double junction electrode and Br-ISE in aqueous solution of NaBr and $Ca(NO_3)_2$ at total ionic strength 6 and 298.2 K.

* reference: Single Junction Electrode

† reference: Double Junction Electrode

‡ reference: Bromide Ion-Selective Electrode

Appendix D

Selectivity Coefficients of Ion–Selective Electrodes

As explained in Chapter 5 and Chapter 7, the separate solutions technique was used to determine the selectivity coefficient of ion-selective electrodes. It was also explained that, using the separate solution technique, two methods can be applied to evaluate selectivity coefficients, one is the equal activity method and the other one is the equal electromotive force method. In the evaluation of the selectivity coefficient presented in Chapter 7, the separate solution method (equal activity method) is used. The details of the derivation of the equations related to selectivity coefficients of NO_{3^-} ISE, Na-ISE and Ca-ISE were presented in Chapter 7. In this appendix numerical values of selectivity coefficients, using calibration lines for each ion-selective electrode in the two respective binaries, are shown. One of these binaries involves the detected ions and the other contains the interfering ions.

Table (D.1) shows the emf values of Na-ISE towards NO_3 -ISE in two separate binary solutions of NaBr and NaNO₃. As shown in Chapter 6, the following calibration line was obtained for the response of Na-ISE against NO_3 -ISE:

 $E(NaNO_3)_{NaNO_3} = 322.68 + 24.59 \ln a(NaBr)$

Table (D.1) shows the values of $K_{NO_3-Br}^{pot}$ at different molalities. An average value of 0.135 is obtained.

Table (D.2) shows the emf values of Na-ISE towards NO_3 -ISE in two separate solutions of NaBr and Ca(NO_3)₂. The following calibration line is obtained for the response of Na-ISE towards NO_3 -ISE in aqueous solution of Ca(NO_3)₂.

$$E(\text{NaNO}_3)_{\text{Ca}(\text{NO}_3)_2} = 120.99 + 7.82 \ln a [\text{Ca}(\text{NO}_3)_2]$$

An average value of 0.707 x 10^{-3} for K_{Ca-Na}^{pot} is obtained at low concentrations of Na and Ca ions.

Finally, Table (D.3) shows the emf values of Ca-ISE towards NO_3 -ISE in two separate solutions of NaNO₃ and Ca(NO₃)₂. As presented in Chapter 6, the following calibration line was obtained for the response of Ca-ISE towards NO₃-ISE at low concentrations of calcium ions.

 $E(Ca(NO_3)_2)_{Ca(NO_3)_2} = 78.435 + 11.429 \ln \alpha(NaNO_3)$

An average value of 9.303 x 10^{-3} for K_{Ca-Na}^{pot} is obtained at low concentrations of Na and Ca ions.

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Table D.1: Selectivity coefficient of NO_3 -ISE towards Br⁻ ions using emf measurements of Na-ISE towards NO_3 -ISE in the two aqueous solutions of NaBr and NaNO₃ at 298.2 K.

Molality	γ_{\pm}	activity	$\ln(a)$	E(NaNO ₃)	E(NaNO ₃)	K _{NO3-Br}
	(exp)	(exp)	(exp)	(exp)	(regr)	_
NaBr	NaBr	NaBr	NaBr	NaBr*	$NaNO_3^{\dagger}$	
0.300	0.710	0.045	-3.093	198.5	246.6	0.141
0.250	0.721	0.032	-3.427	190.3	238.4	0.141
0.200	0.732	0.021	-3.843	179.9	228.2	0.140
0.150	0.754	0.013	-4.359	166.4	215.5	0.136
0.100	0.775	0.006	-5.115	148.8	196.9	0.142
0.090	0.782	0.005	-5.308	144.0	192.1	0.141
0.080	0.790	0.004	-5.523	138.6	186.8	0.141
0.070	0.798	0.003	-5.770	132.5	180.8	0.140
0.060	0.808	0.002	-6.053	125.3	173.8	0.139
0.050	0.819	0.002	-6.391	116.8	165.5	0.138
0.040	0.832	0.001	-6.806	106.1	155.3	0.135
0.030	0.849	0.001	-7.341	92.5	142.2	0.133
0.020	0.870	0.000	-8.103	73.2	123.4	0.130
0.015	0.886	0.000	-8.641	59.5	110.2	0.128
0.010	0.902	0.000	-9.417	40.1	91.1	0.126
0.008	0.910	0.000	-9.845	29.5	80.5	0.125
0.006	0.921	0.000	-10.397	15.6	67.0	0.124
0.005	0.927	0.000	-10.748	6.9	58.3	0.124

* Binary aqueous solution of NaBr

† Binary aqueous solution of NaNO₃

Table D.2: Selectivity coefficient of Na-ISE towards Ca^{++} ions using emf measurements of Na-ISE towards NO₃-ISE in the two aqueous solutions of NaNO₃ and $Ca(NO_3)_2$ at 298.2 K.

Molality	γ_{\pm}	activity	$\ln(a)$	$E(NaNO_3)$	E(NaNO ₃)	K _{Na-Ca}
	(exp)	(exp)	(exp)	(exp)	(regr)	
NaNO ₃	NaNO ₃	NaNO ₃	NaNO ₃	NaNO3*	$Ca(NO_3)_2^{\dagger}$	
0.300	0.666	3.99E-02	-3.221	242.9	95.8	5.05E-04
0.250	0.684	2.92E-02	-3.532	235.5	93.4	5.29E-04
0.200	0.702	1.97E-02	-3.927	225.8	90.3	5.68E-04
0.140	0.737	1.06E-02	-4.543	210.2	85.5	6.47E-04
0.100	0.760	5.78E-03	-5.154	196. 1	80.7	6.96E-04
0.090	0.762	4.70E-03	-5.360	191.2	79.1	7.18E-04
0.080	0.771	3.80E-03	-5.572	185.8	77.4	7.52E-04
0.070	0.782	3.00E-03	-5.810	180.0	75.6	7.83E-04
0.060	0.793	2.26E-03	-6.091	173.0	73.4	8.28E-04
0.050	0.811	1.64E-03	-6.410	164.4	70.9	9.04E-04
0.040	0.822	1.08E-03	-6.830	155.1	67.6	9.36E-04
0.030	0.841	6.37E-04	-7.359	141.9	63.4	1.04E-03
0.020	0.867	3.01E-04	-8.109	122.8	57.6	1.22E-03
0.015	0.882	1.75E-04	-8.651	109.9	53.3	1.33E-03
0.010	0.900	8.10E-05	-9.421	90.7	47.3	1.54E-03
0.008	0.908	5.28E-05	-9.850	80.0	44.0	1.68E-03
0.006	0.919	3.04E-05	-10.401	66.4	39.7	1.86E-03
0.005	0.926	2.14E-05	-10.750	57.7	36.9	1.99E-03

* Binary aqueous solution of NaNO₃

 \dagger Binary aqueous solution of Ca(NO₃)₂

Table D.3: Selectivity coefficient of Ca-ISE towards Na⁺ ions using emf measurements of Ca-ISE towards NO_3 -ISE in the two aqueous solutions of NaNO₃ and Ca(NO₃)₂ at 298.2 K.

Molality	γ_{\pm}	activity	$\ln(a)$	$E[Ca(NO_3)_2]$	$E[Ca(NO_3)_2]$	K ^{pot} _{Ca-Na}
	(exp)	(exp)	(exp)	(exp)	(regr)	
NaNO ₃	NaNO3	NaNO ₃	NaNO ₃	NaNO ₃ *	$Ca(NO_3)^{\dagger}$	
0.300	0.666	3.99E-02	-3.221	-105.2		-
0.250	0.684	2.92E-02	-3.532	-107.2	-	-
0.200	0.702	1.97E-02	-3.927	-112.8	-	-
0.140	0.737	1.06E-02	-4.543	-120.3	-	-
0.100	0.760	5.78E-03	-5.154	-127.1		-
0.090	0.762	4.70E-03	-5.360	-130.3	-	-
0.080	0.771	3.80E-03	-5.572	-132.9	-	-
0.070	0.782	3.00E-03	-5.810	-137.2	~	
0.060	0.793	2.26E-03	-6.091	-138.3	-	-
0.050	0.811	1.64E-03	-6.410	-144.6	5.170	1.2E-03
0.040	0.822	1.08E-03	-6.830	-148.1	0.377	2.1E-03
0.030	0.841	6.37E-04	- 7.3 59	-155.1	-5.676	3.3E-03
0.020	0.867	3.01E-04	-8.109	-165.2	-14.248	6.1E-03
0.015	0.882	1.75E-04	-8.651	-170.4	-20.432	1.1E-02
0.010	0.900	8.10E-05	-9.421	-181.4	-29.238	2.0E-02
0.008	0.908	5.28E-05	-9.850	-186.7	-34.137	3.0E-02
0.006	0.919	3.04E-05	-10.401	-194.6	-40.437	4.6E-02
0.005	0.926	2.14E-05	-10.750	-200.3	-44.431	5.6E-02

 \star Binary aqueous solution of NaNO₃

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 \dagger Binary aqueous solution of Ca(NO₃)₂

Appendix E

Calculation of Molalities of Salts in a Ternary System with Constant Total Ionic Strength

In principle when two binary electrolyte solutions of similar ionic strength, I, are mixed, the total ionic strength of the prepared ternary system is the same as ionic strength of the individual binaries. Table (E.1) shows the variable properties of binary solutions. The molalities of salts in a ternary system composed of binaries with given volume and molality can be evaluated as follows,

• The weight percent of each salt in the respective binaries is calculated as,

$$\omega_{i} = \frac{m_{i} M_{i}}{1000 + m_{i} M_{i}} \times 100$$
(E.1)

• Having the weight percent of each salt permits the calculation of the density of each binary using the CRC Handbook or a similar other source of density data. Then the molarity of each binary can be obtained by having its molality and density as [116]

$$c_{i} = \frac{m_{i}\rho_{i}}{1 + 0.001m_{i}M_{i}} \tag{E.2}$$

• Having the volume and the molarity of the binary solution allows the evaluation of the number of moles of the salt in the given binary as

$$n_{i} = c_{i} V_{i} \tag{E.3}$$

Legend	Binary "1"	Binary "2"
molality	m ₁	m2
molarity	c 1	c ₂
density	ρ_1	ρ_2
molecular weight	M ₁	M ₂
of electrolyte		
volume		V ₂
weight percent	ω_1	ω_2
moles of electrolyte	n ₁	n ₂
weight of solvent	W_1	W2

Table E.1: Variable properties of binary electrolyte solutions

then, the weight of the solvent associated with the each binary solution can be obtained as,

$$W_i = \rho_i V_i - c_i V_i M_i \tag{E.4}$$

• Finally, knowing the number moles of each salt and the weight of the solvent associated with each binary permits the computation of the molalities of salts in the ternary system as,

$$m_1 = \frac{1000 n_1}{\rho_1 V_1 + \rho_2 V_2 - c_1 V_1 M_1 - c_2 V_2 M_2}$$
(E.5)

$$m_2 = \frac{1000 n_2}{\rho_1 V_1 + \rho_2 V_2 - c_1 V_1 M_1 - c_2 V_2 M_2}$$
(E.6)

Therefore, the molalities of the individual salts can be obtained in a multicomponent system which is prepared by mixing n binaries with the same ionic strength using the following relation.

$$m_{i} = \frac{1000 n_{i}}{\sum_{1}^{n} \rho_{i} V_{i} - \sum_{1}^{n} c_{i} V_{i} M_{i}}$$
(E.7)