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Phase Equilibria in Electrolyte Systems

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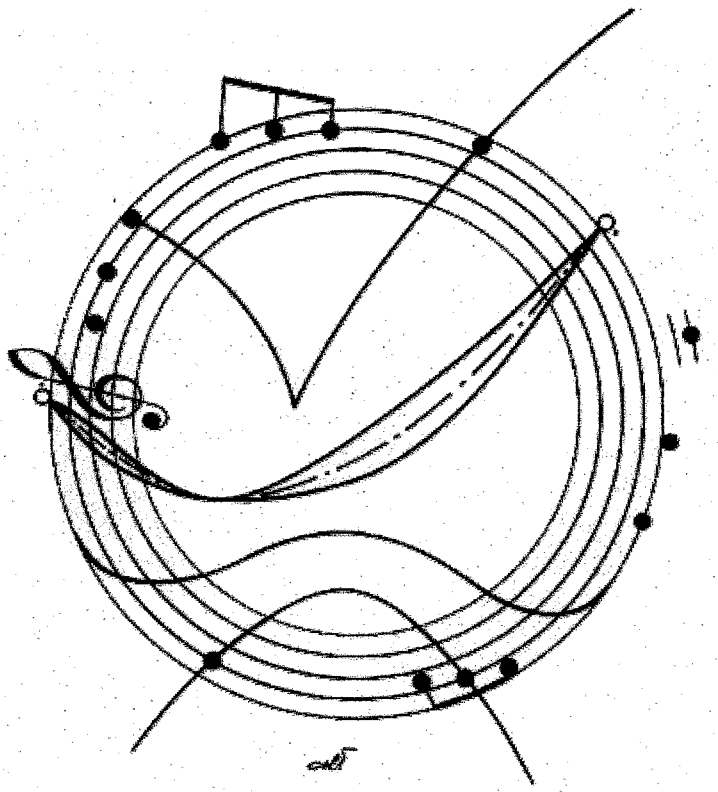
To my Parents



Believing means liberating the indestructible element in oneself,
or, more accurately, being indestructible or, more accurately, being.

Franz Kafka

Abstract

The main objectives of this work are the study of solid-liquid equilibrium of salts in pure and mixed solvents, and of biomolecules, such as amino acids and peptides, in water.

The correlation and prediction of properties for mixtures containing charged electric species, the electrolytes, is of great relevance for the chemical industry. A brief discussion about the whole interest of this work and the need of concentrating efforts to develop accurate models for electrolyte systems is initially focused. The fundamental concepts of electrolyte thermodynamics and industrial examples where electrolytes play an important role are given. The available different models to correlate and/or predict properties and phase equilibria for this kind of mixtures are reviewed and compared.

An isothermal analytical method, which has been implemented to measure salt solubilities, is described in detail. The experimental solubilities obtained for NaCl, KCl, NaBr and KBr, in the pure solvents water, methanol, ethanol and in the mixed solvents water/methanol, water/ethanol and methanol/ethanol in the temperature range between 25 °C and 80 °C are given.

The new experimental data is used together with additional information published by other authors, concerning solid-liquid equilibrium of salts in pure and mixed solvents and osmotic coefficients in pure solvents, in order to establish an extensive and reliable database. This is adopted for the development of consistent thermodynamic models.

Two UNIQUAC based models are suggested: the UNIQUAC + Pitzer-Debye-Hückel model, and the UNIQUAC model with linear temperature dependent solvent/salt parameters. A new developed approach for correlating salt solubilities, based on the symmetric convention of normalization of the activity coefficients and on the mole fraction concentration scale on ionized basis is presented. In this way, it is possible the direct access to the salt solubility product in terms of its calorimetric properties such as the melting temperature, enthalpy of fusion and heat capacity change. The capabilities of these models for the correlation and prediction of solid-liquid equilibrium and other thermodynamic properties are discussed. The results indicate that this procedure and these models are satisfactory for solid-liquid equilibrium calculations.

The work on weak electrolytes consists of the development of a new group-contribution method. This includes two terms: the UNIFAC model to account for the short-range interaction forces, and a Debye-Hückel expression for the long-range forces. New UNIFAC groups have been assigned to describe the amino acids and peptides studied, and the chemical equilibrium is taken into account simultaneously with the physical equilibrium. Using this approach, the temperature and pH effects on the solubilities of amino acids in aqueous solutions are taken into consideration. This model predicts very successfully the pH influence on the solubilities of amino acids and therefore may be used for engineering purposes.

Resumo

Este trabalho tem como principais objectivos o estudo do equilíbrio sólido-líquido de sais em solventes puros e mistos, e de biomoléculas , como aminoácidos e peptídeos, em água.

A correlação e previsão de propriedades termodinâmicas de misturas contendo espécies iónicas, os electrólitos, é de grande importância na indústria química. Apresenta-se inicialmente uma breve introdução do interesse geral deste trabalho e foca-se a necessidade de desenvolver esforços na modelação deste tipo de sistemas. Em seguida, efectua-se uma revisão dos conceitos fundamentais da termodinâmica de electrólitos usados neste estudo e apresentam-se exemplos de aplicações industriais em que a presença de espécies iónicas é frequente. Os modelos já disponíveis para a correlação e/ou previsão de propriedades e equilíbrio de fases para este tipo de misturas são também comparados.

A determinação experimental das solubilidades de NaCl, KCl, NaBr e KBr, nos solventes puros água, metanol e etanol e nos solventes mistos água/metanol, água/etanol e metanol/etanol, é realizada recorrendo a um método analítico isotérmico, que envolve um processo de amostragem inovador. A gama de temperaturas coberta é de 25 °C a 80 °C.

Os novos dados experimentais, conjuntamente com informação adicional publicada por outros autores relativa a equilíbrio sólido-líquido de sais em solventes puros e mistos, e de coeficientes osmóticos, são utilizados para constituir uma base de dados consistente e extensa. Esta é adoptada para o desenvolvimento de modelos termodinâmicos.

São estabelecidos dois modelos baseados na equação UNIQUAC: UNIQUAC + Pitzer-Debye-Hückel e UNIQUAC com parâmetros solvente/sal linearmente dependentes da temperatura. Desenvolve-se um novo procedimento para correlacionar as solubilidades dos sais. Este baseia-se na convenção simétrica de normalização dos coeficientes de actividade e na escala de concentração em fracção molar em base ionizada. Deste modo, é possível calcular directamente o produto de solubilidade do sal em termos das suas propriedades calorimétricas, como a temperatura de fusão, a entalpia de fusão e a diferença das capacidades caloríficas entre o sal puro no estado sólido e no estado líquido. São ainda analisadas as potencialidades destes modelos na correlação e na previsão de equilíbrio sólido-líquido e de outras propriedades termodinâmicas. Os resultados mostram que este procedimento e tais modelos são bastante adequados para o cálculo de equilíbrio sólido-líquido.

Relativamente a electrólitos fracos, propõe-se um novo método de contribuições de grupo. Este inclui dois termos: o modelo UNIFAC para descrever as interacções de curto alcance, e uma expressão de Debye-Hückel para traduzir as interacções de longo alcance. Definem-se novos grupos funcionais para a descrição das moléculas dos aminoácidos e dos peptídeos. O equilíbrio químico é considerado em simultâneo com o equilíbrio físico. Assim, pode avaliar-se a influência da temperatura e do pH na solubilidade de aminoácidos em solução aquosa. Este modelo prevê com elevado rigor o efeito do pH na solubilidade de aminoácidos e pode ser usado em cálculos de simulação de processos de separação.

Résumé

L'objectif principal de ce travail est l'étude des équilibres liquide-solide de sels dans des solvants purs et mixtes ainsi que de biomolécules tels que des acides aminés et des peptides dans l'eau.

La corrélation et la prédiction des propriétés de solutions électrolytiques contenant des espèces chargées est essentiel pour l'industrie chimique. Une première partie de ce mémoire est consacrée à une courte discussion sur l'intérêt de ce travail et sur la nécessité de concentrer nos efforts sur le développement de modèles électrolytiques précis. Apès une description des concepts fondamentaux de la thermodynamique des électrolytes, nous donnons des exemples industriels dans lesquels les électrolytes jouent un rôle important. Les différents modèles décrits dans la littérature et permettant de corréler et/ou prédire les propriétés et les équilibres de phases de tels systèmes sont passés en revue et comparés.

Une méthode analytique isotherme, développée pour mesurer la solubilité des sels est alors décrite en détail. Cette méthode a été utilisée por mesurer les solubilités de NaCl, KCl, NaBr et KBr dans des solvants purs tels que l'eau, le méthanol, l'éthanol ainsi que dans des solvants mixtes tels que des mélanges eau/méthanol, eau/éthanol et méthanol/éthanol dans un domaine de température allant de 25 °C à 80 °C.

Les données expérimentales ainsi acquises ont été associées à d'autres données de la littérature concernant à la fois des données d'équilibre liquide-solide de sels dans des solvants purs et mixtes et des données de coefficients osmotiques dans des solvants purs afin de disposer d'une base de données complète et fiable qui servira à la mise au point de modèles thermodynamiques.

Deux modèles utilisant UNIQUAC ont été retenus. Le premier combine le modèle UNIQUAC et le modèle de Pitzer-Debye-Hückel. Le second est le modèle UNIQUAC proprement dit dans lequel les paramètres solvant/sel sont des fonctions linéaires de la température. Une nouvelle approche, reposant sur la convention symétrique et utilisant les fractions molaires des espèces ioniques comme variable de composition a été dévelopée afin de corréler la solubilité des sels. De cette façon, le produit de solubilité peut directement être calculé à partir de données calorimétriques telles que: la température, l'enthalpie et la capacité calorifique de fusion. Ces deux modèles ont été utilisés pour prédire et corréler des équilibres liquide-solide et d'autres propriétés thermodynamiques. Les résultats obtenus indiquent que ces deux modèles restituent de façon satisfaisante les équilibres liquide-solide.

Une nouvelle méthode de contributions de groupes a été développée en vue de représenter les propriétés thermodynamiques des électrolytes faibles. L'expression mise au point associe le modèle UNIFAC qui prend en compte les interactions à courte distance avec l'expression de Debye-Hückel qui tient compte des interactions à longue distance. De nouveaux groupes UNIFAC ont du être définis afin de décrire les acides aminés et les peptides étudiés. De plus, il a été nécessaire de prendre en compte simultanément les équilibres physiques et chimiques, de manière à décrire les effets du pH et de la température sur la solubilité des acides aminés en solution aqueuse. Le modèle ainsi défini, prédit parfaitement l'influence du pH sur la solubilité des acides aminés et peut donc être utilisé à des fins industrielles.

Riassunto

I principali obiettivi di questo lavoro sono lo studio dell'equilibrio solido-liquido di sali in solventi puri e misti e di biomolecole, come amminoacidi e peptidi, in acqua.

La correlazione e previsione di proprietà termodinamiche di miscele che contengono specie ioniche, gli elettroliti, hanno una grande inportanza nell'industria chimica. All'inizio è presentata una breve introduzione sull'interesse generale di questo lavoro e si mette a fuoco la necessità di sviluppare degli sforzi nel modellare questo tipo di sistemi. Dopo si effettua una revisione dei concetti fondamentali della termodinamica di elettroliti usati in questo studio e si presentano esempi di applicazioni industriali in cui la presenza di specie ioniche è frequente. Sono anche confrontati i modelli già disponibili per la correlazione e/o previsione di proprietà e equilibrio di fasi per questo tipo de miscele.

La determinazione sperimentale delle solubilità di NaCl, KCl, NaBr e KBr, nei solventi puri acqua, metanolo e etanolo e nei solventi misti acqua/metanolo, acqua/etanolo e metanolo/etanolo, è realizzata tramite il ricorso a un metodo analitico isotermico che implica un processo di campionatura innovativo. La gamma di temperatura coperta è da 25 °C a 80 °C.

I nuovi dati sperimentali, insieme con informazione aggiuntiva pubblicata da altri autori relativa all'equilibrio solido-liquido di sali in solventi puri e misti e di coefficienti osmotici, sono utilizzati per costruire una banca dati consistente ed estesa, che è adottata per lo sviluppo di modelli termodinamici.

Sono stabiliti due modelli basati sull'equazione UNIQUAC: UNIQUAC + Pitzer-Debye-Hückel e UNIQUAC con parametri solvente/sale linearmente dipendenti dalla temperatura. Si sviluppa un nuovo procedimento per mettere in correlazione le solubilità dei sali. Questo si basa sulla convenzione simmetrica di normalizzazione dei coefficienti di attività e sulla scala di concentrazione in frazione molare su base ionizzata. È possibile, in tal modo, calcolare direttamente il prodotto di solubilità del sale in termini delle sue proprietà calorimetriche, come la temperatura di fusione, l'entalpia di fusione e la differenza delle capacità calorifiche tra il sale puro allo stato solido e allo stato liquido. Sono inoltre analizzate le potenzialità di questi modelli nella correlazione e nella previsione dell'equilibrio solido-liquido e di altre proprietà termodinamiche. I risultati mostrano che questo procedimento e tali modelli sono abbastanza adeguati per il calcolo di equilibrio solido-liquido.

Relativamente a elettroliti deboli si propone un nuovo metodo di contributi di gruppo. Questo include due termini: il modello UNIFAC per descrivere le interazioni di corta gettata e una espressione di Debye-Hückel per tradurre le interazioni di lunga gettata. Si definiscono nuovi gruppi funzionali per la descrizione delle molecole degli amminoacidi e dei peptidi. L'equilibrio chimico è considerato allo stesso tempo con l'equilibrio fisico. Si può valutare così l'influenza della temperatura e del pH nella solubilità di amminoacidi in soluzione acquosa. Questo modello prevede con elevato rigore l'effetto del pH nella solubilità di amminoacidi e può essere usato in calcoli di simulazioni di processi di separazione.

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INTRODUCTION

1. Introduction

1.1 Importance and Motivation

The thermodynamics of electrolyte solutions has been, during the last years, one major area of research. In fact, it is very common to find electric charged species in many natural and industrial processes. However, much of the experimental and modelling work has been carried out for aqueous systems, while for mixed solvent electrolyte systems only the vapour-liquid equilibrium has received considerable attention.

The importance of salts as alternative separating agents for azeotropic or extractive distillations is well known. In spite of that, the number of large-scale industrial applications of extractive distillation by salt effect to date has been reduced. The main reasons for this lie in the extreme complexity to describe rigorously the liquid phase and also on the fact that salt precipitation may occur inside the column. Therefore, experimental and thermodynamic modelling of solid-liquid equilibrium in electrolyte systems are fundamental for the understanding of the interactions in the liquid phase, as well as for the design, optimization, and scale-up separation processes.

Another research area where electrolytes play an important role is in biotechnology. Specifically, the development of efficient methods for the separation and concentration of biomaterials, like amino acids and peptides, which are weak electrolytes, needs the

knowledge of fundamental physical properties of bioproduct mixtures such as the solubilities and activity coefficients of the biomolecules in water.

1.2 Objectives

The main objectives of this thesis are the study of solid-liquid equilibrium in electrolyte systems, namely of salts in pure and mixed solvents and of biomolecules in water. In this way, both strong and weak electrolytes thermodynamics are focused.

In chapter 2 the fundamental tools for the thermodynamics of electrolyte mixtures are given, as well as some important examples where electrolytes play an important role.

The critical review of the available thermodynamic models is presented and their capabilities to correlate and/or predict thermodynamic properties and phase equilibria are briefly discussed. Comparisons about the performance of each model and some computed examples are also given.

Chapter 3 deals with the experimental measurement of salt solubility. In fact, until nowadays little work has been carried out in this area, since the majority of the studies are only concerned with vapour-liquid equilibrium. The techniques usually applied are compared and the choice of an analytic technique for the measurements is completely justified together with details of the whole procedure.

The experimental results obtained for the solubilities of NaCl, KCl, NaBr, KBr, in the pure solvents water, methanol, ethanol, and in the mixed solvents water/methanol, water/ethanol, and methanol /ethanol in the temperature range between 298.15 and 353.15 K are given. A critical analysis of the obtained data is also displayed.

Chapter 4 presents the modelling work for the solid-liquid equilibrium of salts in pure and mixed solvents. A new formulation, based on the symmetric convention for the normalization of the activity coefficients is applied for all the components, with the reference state of the salt being the pure fused salt at the solution temperature. Using this approach, the solubility product is directly calculated from the knowledge of some calorimetric properties such as the melting temperature, the enthalpy of fusion, and the heat capacity change.

A reliable database founded on salt solubility data measured in this work and selected from the open literature, together with osmotic coefficient data is established to enable, at the same time, the estimation of parameters for the thermodynamic models developed and their validation.

Two models are proposed: one combines the original UNIQUAC equation with a Pitzer-Debye-Hückel expression to take into account the long-range interaction forces. The other model only considers the short-range forces through the UNIQUAC equation with linear temperature dependent salt/solvent interaction parameters. A critical evaluation of both suggested models is given as well as their versatility to represent other type of equilibrium data or prediction capabilities.

Chapter 5 focuses the development of a group-contribution UNIFAC method for the study of the solubility of amino acids in water, which behave as weak electrolytes. The model developed, is based on the available experimental values for the activity coefficients of amino acids and peptides in water, and accounts simultaneously the physical and the chemical equilibrium in order to study the influence of temperature and pH on the solubilities.

The main conclusions of this work are presented in chapter 6, where suggestions for future work are also addressed.

Chapter 2

THERMODYNAMICS OF ELECTROLYTE SOLUTIONS

2. Thermodynamics of Electrolyte Solutions

2.1 Introduction

Electrolyte solutions can be found in many natural and industrial processes. Therefore, it is not surprising that during the last few decades much attention has been devoted to experimental and theoretical studies in this area. However, there are some difficulties arising from the lack of well-defined thermodynamic functions because there are no standards universally accepted for some basic concepts. Thus, in this chapter initially, it is shown the importance of the study of these systems from an industrial point of view. After, the fundamental tools for the thermodynamics of electrolyte solutions, as well as a revision concerning the most useful models for the correlation or/and prediction of thermodynamic properties in this kind of systems, are given.

2.1.1 Short Historical Preview

According to the historical studies of Underwood and Forbes, it was during the 12th century, in Italy, probably around Salerno, that for the first time the production of a strong alcohol from water/ethanol solutions, like wine, by distillation with the addition of quick-lime, sulphur, tartar and "white common salt", was reported (Furter, 1977). Such a process was applied for the production of strong spirits and to manufacture explosive mixtures for military purposes.

"The first indisputable preparation of absolute ethanol" was carried out during 1796, when the German chemist Lowitz, in St. Petersburg, distilled strong alcohol with burnt potassium carbonate. The measurements of vapour pressures in the important water/alcohol systems with salts, around the turn of the 20th century, and the discovery that the salt effect on the vapour composition could be related to salt solubilities in the pure liquid components, were the first systematised studies in this field conducted by W. Lash Miller in Canada and I. A. Kablukov in Russia. After this, an enormous amount of work has been published (Furter and Cook, 1967; Furter, 1977), mainly on experimental measurements for vapour-liquid equilibrium (VLE).

However, thermodynamics of electrolyte systems in mixed solvents have received attention only recently, when compared to earlier developments carried out for aqueous systems: it was during the seventies, that efforts were made to establish reliable and systematic measurements. The works by J. R Alvarez González in Spain, William F. Furter in Canada and S. Ohe in Japan represented, among others, great improvements for further developments in the following years up to date.

2.1.2 Industrial Applications

Many examples can be given about the industrial applications of electrolytes. In fact, it is very common to find electric charged species in several separation processes in chemical, petroleum, hydrometallurgical, biochemical, pharmaceutical or food industries. Some examples are:

Absorption for the removal of acid gases such as carbon dioxide and hydrogen sulfide from effluent gas streams, avoiding atmospheric pollution, is a typical example where the solubility of weak electrolyte gases in aqueous solutions has to be taken into account (Maurer, 1983).

Extractive crystallization, a recently developed precipitation process to selectively separate targeted salts from seawater, formation water and groundwater by the addition of an organic solvent as the precipitation agent (Bader, 1998) is an application under attention. A practical example is the crystallization of sodium nitrate using isopropanol. As can be seen in Figure 2.1 addition of 500 g of isopropanol to 1 kg of a sodium nitrate saturated aqueous solution at 313.15 K allows a salt recovery of around 68%.

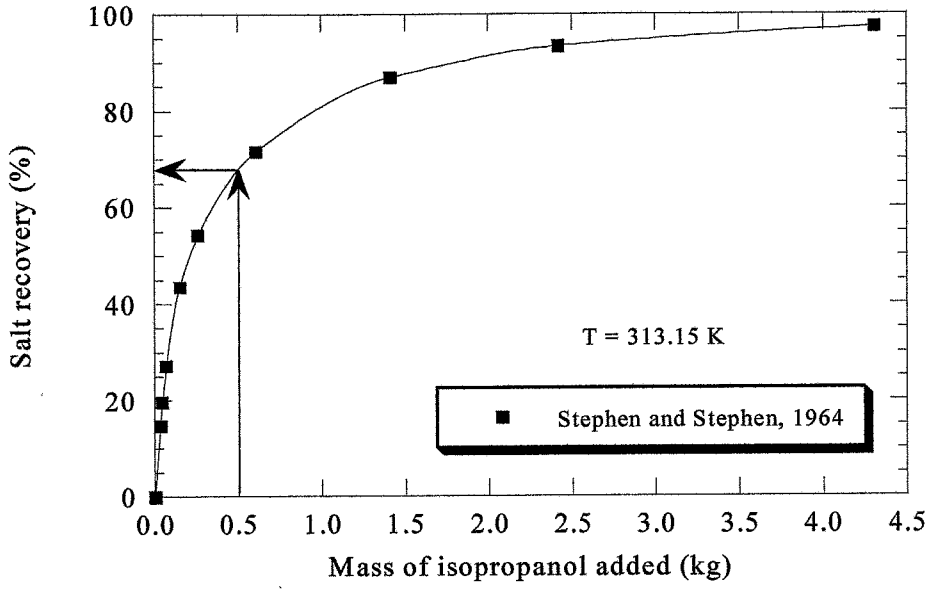

Figure 2.1 *Dependency of potassium nitrate recovery on the added mass of isopropanol.*

Fractional crystallization, a process in which several salts are separated as pure phases from a multicomponent mixture, has been used in the production of fertilizers like ammonium phosphate, ammonium nitrate or potassium sulphate. The annual production of each exceeds 1 million-ton and its importance is evident. The fractional crystallization process has been applied, for instance, in the production of potassium sulphate and sodium chloride from sodium sulphate and potassium chloride aqueous solutions (Thomsen, 1997).

Extractive distillation using salt as extractive agent. Systems exhibiting azeotropic behaviour can only be separated using an agent, which is able to significantly alter the equilibrium relations. The introduction of a salt into a solvent mixture results in a change in the relative volatility of the solvents, and therefore salts are potential separation agents.

The isopropanol/water system presents an azeotrope. The conventional separation process involves the use of benzene to break it. Figure 2.2 shows that calcium chloride has also the same ability, even at low salt concentrations. In fact, Ishikawajima-Harima Heavy Industries (IHI) Company in Japan developed a process for the production of isopropanol from aqueous solutions using calcium chloride. In a plant producing 7300 ton/year the capital and operation costs are, respectively, 56% and 45% lower than those obtained for the conventional process (Furter, 1992).

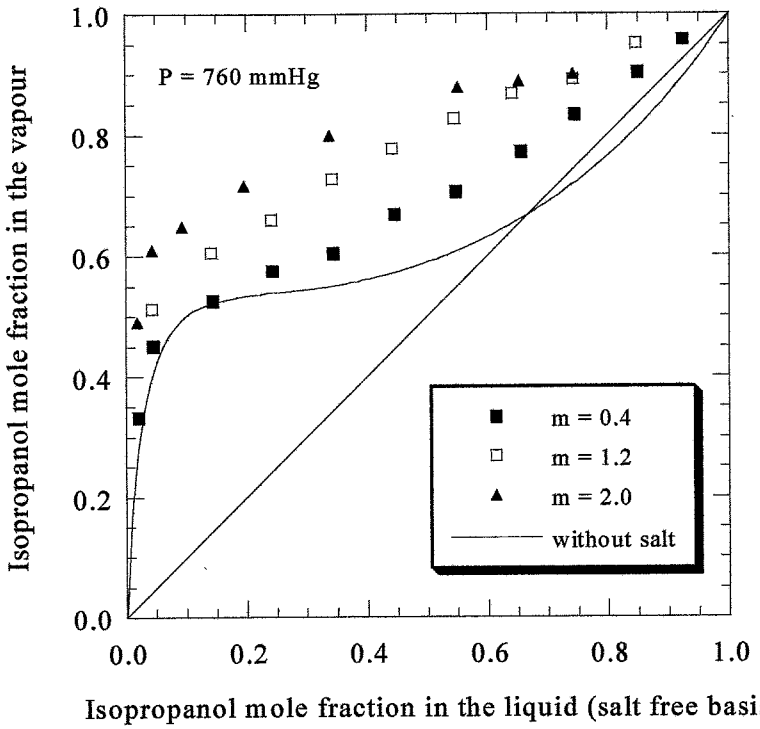

Figure 2.2 *Vapour-liquid equilibrium for the system water/isopropanol/$CaCl_2$ at different salt molalities (Ohe, 1991).*

Liquid-liquid extraction to recover biomolecules such as enzymes from a fermentation broth (Kula et al., 1982; Groβmann and Maurer, 1995) using aqueous two-phase systems by adding a hydrophylic polymer and a strong electrolyte, or for instance to purify amino acids using a mixture of an organic solvent and a quaternary ammonium salt (Hano et al., 1991).

Precipitation of globular proteins, which normally are polyelectrolytes, from an aqueous solution by addition of salts (Prausnitz, 1995).

2.2 Fundamental Concepts and Definitions

The theory of electrolyte solutions starts in 1887 with the brilliant discovery of Svanté Arrhenius who found, that certain solutes dissociate into electrically charged species, the ions. In this way, electrolytes are usually classified in terms of their degree of dissociation in solution: those undergoing a total dissociation into cations and anions are called strong electrolytes, while the ones that participate in different chemical reactions, like ion association, are named weak electrolytes.

This classification has no definite boundaries, because the degree of dissociation depends, among others, on the type of solvent and solute concentration. For instance, potassium bromide is a strong electrolyte in water while in acetic acid it is not.

Thermodynamics of electrolyte solutions differs significantly from non-electrolyte thermodynamics due to the presence of ionic species. The structure of the liquid phase is much more difficult to describe; the long-range nature of electrostatic forces is responsible, for instance, for the strong deviation from ideality in dilute solutions. Some other aspects are different, like the concentration scale and standard states used, which are usually source of confusion, and some restraints, like the electroneutrality, should be taken into account. Thus, it is not an easy task the extension of a thermodynamic framework for non-electrolytes to electrolytes.

Robinson and Stokes (1970) give a very good insight into this scientific field in a very important and famous book on electrolyte solutions. More recently, the books by Pitzer (1991), Barthel et al. (1998) and Prausnitz et al. (1998) show good improvements for the last developments in this area.

2.2.1 Concentration Scales

The concentration scales commonly used to express the composition of an electrolyte solution are:

a. The molality scale

The molality (m_i) is defined as the number of moles (n_i) of solute i per kilogram of solvent:

$$m_i = \frac{n_i}{\sum_{m=1}^{N_{solv}} n_m M_m} \tag{2.1}$$

where n_m is the number of moles of the solvent m, M_m is its molecular weight (kg/mol) and N_{solv} is the total number of solvents in solution.

b. The molarity scale

The molarity (c_i) is defined as the number of moles of solute i per liter of solution:

$$c_i = \frac{n_i}{V} \tag{2.2}$$

where V is the volume of the system in dm^3.

c. The mole fraction scale

This is the most used concentration unit for non-electrolyte systems. The mole fraction (x_j) of a any species j is defined by:

$$x_j = \frac{n_j}{\sum_{j=1}^{N_{spec}} n_j} \tag{2.3}$$

where n_j is the number of moles of the species j, and N_{spec} is the number of species, solutes and solvents, in solution.

In electrolyte thermodynamics it is also very common to use the solvent mole fraction on a solute free basis, defined according to:

$$x'_m = \frac{n_m}{\sum_{m=1}^{N_{solv}} n_m} \tag{2.4}$$

Concerning these concentration units it is worth to mention that the molarity scale is being left out since it strongly depends on the temperature of the solution, which makes it useless for calculation purposes. The molality scale is not suitable for high solute concentrations because it tends to infinite as the ratio solvent/solute tends to zero. Moreover, despite of the chosen scale the anion or cation concentrations are dependent in view of the electroneutrality of the solution requirement.

The conversions between these different units are easily derived from their definitions and are given in Table 2.1, where N_{solu} and ρ are the numbers of solutes (ions) in solution and the density of the solution (kg/dm^3), respectively.

Table 2.1 Conversions between different concentration scales.

	To	m_i	c_i	x_i
From	m_i	–	$\dfrac{\rho m_i}{1+\sum_{l=1}^{N_{solu}} m_l M_l}$	$\dfrac{m_i}{\sum_{l=1}^{N_{solu}} m_l + 1\Big/\sum_{m=1}^{N_{solv}} x_m' M_m}$
	c_i	$\dfrac{c_i}{\rho - \sum_{l=1}^{N_{solu}} c_l M_l}$	–	$\dfrac{c_i}{\sum_{l=1}^{N_{solu}} c_l + \dfrac{\rho - \sum_{l=1}^{N_{solu}} c_l M_l}{\sum_{m=1}^{N_{solv}} x_m' M_m}}$
	x_i	$\dfrac{x_i}{\sum_{m=1}^{N_{solv}} x_m M_m}$	$\dfrac{\rho x_i}{\sum_{j=1}^{N_{spec}} x_j M_j}$	–

2.2.2 Thermodynamics for Phase Equilibria

The phase equilibrium problem is mathematically expressed with the aid of the chemical potential (μ_j) of a component j, which is defined according to:

$$\mu_j = \left(\frac{\partial G}{\partial n_j}\right)_{P,T,n_{k\neq j}} \tag{2.5}$$

G is the total Gibbs energy of the solution. Both these properties are related to measurable variables: absolute temperature (T), pressure (P), and composition or number of moles.

To simplify the abstract equation for the chemical potential, G. N. Lewis first considered the chemical potential for a pure, ideal gas and, by analogy, then generalized it to an isothermal change for any component in any system, whether solid, liquid, or gas, pure or mixed, ideal or not, by the introduction of fugacity ($\hat{f}_j$) of component j,

$$d\mu_j = RT \ln \hat{f}_j \tag{2.6}$$

where R is the ideal gas constant.

Integrating this differential equation between a chosen standard state and a real solution state:

$$\mu_j = \mu_j^{ref} + RT \ln\left(\frac{\hat{f}_j}{\hat{f}_j^{ref}}\right) = \mu_j^{ref} + RT \ln a_j \tag{2.7}$$

where μ_j^{ref} and $\hat{f}_j^{ref}$ are the chemical potential and fugacity at the standard state, respectively. The ratio $\hat{f}_j / \hat{f}_j^{ref}$ is called activity (a_j) indicating how active is the component relatively to its standard state. In electrolyte solutions different standard states can be adopted.

2.2.3 Standard States and Activity Coefficients

The solvent standard state, represented by the superscript $\circ$, is always the pure liquid at the system temperature and pressure. Thus, for a solvent m, equation 2.7 becomes:

$$\mu_m = \mu_m^{\circ} + RT \ln a_m \tag{2.8}$$

The activity can be written as,

$$a_m = f_m x_m \tag{2.9}$$

where f_m is the symmetric rational activity coefficient of the solvent, since for this standard state the mole fraction concentration scale is always adopted. In the real solution the activity coefficients are normalized according to the symmetric convention:

$$f_m \to 1 \text{ as } x_m \to 1 \tag{2.10}$$

For the solute (ions) this standard state can also be used, but is merely hypothetical since at the temperature and pressure of the system, the solute is usually in the solid state and not in the liquid state.

Another standard state for the solute, which is widely used, and denoted in this work by $\bullet$, is the solute in a hypothetical ideal dilute solution at a fixed concentration, usually unit for any concentration scale, at system temperature and pressure. By analogy, equation 2.7 is,

$$\mu_i = \mu_i^{\bullet,\theta} + RT \ln a_i^{\theta} \tag{2.11}$$

The activity can be written in some different ways, depending on the concentration scale (θ) adopted:

$$a_i^x = f_i^* x_i \tag{2.12}$$

$$a_i^m = \gamma_i^* m_i \tag{2.13}$$

$$a_i^c = y_i^* c_i \tag{2.14}$$

In the real solution, the unsymmetric rational (f^*), molal (γ^*) and molar (y^*) activity coefficients are normalized in accordance to the unsymmetric convention by:

$$\begin{matrix} f_i^* \to 1 \\ \gamma_i^* \to 1 \\ y_i^* \to 1 \end{matrix} \quad \text{as} \quad \sum_{l=1}^{N_{solu}} \theta_l \to 0 \tag{2.15}$$

This means that, for an ideal solution in the sense of Henry's law, any activity coefficient of a component i is equal to one at infinite dilution.

Much of the confusion in the study of electrolyte solutions arises from all these different possible activity coefficients. Most of the tabulated values for activity coefficients are molal unsymmetric ones, while for calculation purposes the rational symmetric ones are easily obtained from the thermodynamic models. Fortunately, as for the concentration scales, it is easy to convert between symmetric and unsymmetric conventions of normalization as well as between different concentration scales.

The value of the standard chemical potential, as suggested by equation 2.11, depends both on the convention of normalization and on the concentration scale used. On the contrary, the chemical potential of an ion at a given composition is only dependent of the temperature and pressure. It is then possible to write the following equality:

$$\mu_i = \mu_i^{\bullet,x} + RT \ln\left(f_i^* x_i\right) = \mu_i^\circ + RT \ln\left(f_i x_i\right) \tag{2.16}$$

or,

$$\frac{\mu_i^{\bullet,x} - \mu_i^\circ}{RT} = \ln\left(\frac{f_i}{f_i^*}\right) \tag{2.17}$$

Taking the limit, when $\sum_{l=1}^{N_{solu}} x_l \to 0$, for all temperatures and pressures, $f_i^* \to 1$ and $f_i \to f_i^\infty$ and equation 2.17 becomes,

$$\frac{\mu_i^{\bullet,x} - \mu_i^\circ}{RT} = \lim_{\sum_{l=1}^{N_{solu}} x_l \to 0} \ln\left(\frac{f_i}{f_i^*}\right) = \ln f_i^\infty \tag{2.18}$$

where f_i^∞ is the symmetric rational activity coefficient of ion i at infinite dilution. By comparing eqs. 2.17 and 2.18, one obtains equation 2.19, relating the rational symmetric and unsymmetric activity coefficients:

$$\frac{f_i}{f_i^*} = f_i^\infty \tag{2.19}$$

Similar equations can be found for the symmetric and unsymmetric activity coefficients at any other concentration scale. In Appendix A identical derivations are presented for the conversions between the activity coefficients at different concentration scales. The results are given in Table 2.2.

Table 2.2 Conversions between molal, molar, and rational unsymmetric activity coefficients.

	To	γ_i^*	y_i^*	f_i^*
From	γ_i^*	–	$\frac{\rho_\circ}{\rho}\left(1+\sum_{l=1}^{N_{solu}} m_l M_l\right)\gamma_i^*$	$\left(1+\sum_{l=1}^{N_{solu}} m_l \sum_{m=1}^{N_{solv}} x_m' M_m\right)\gamma_i^*$
	y_i^*	$\frac{\rho - \sum_{l=1}^{N_{solu}} c_l M_l}{\rho_\circ} y_i^*$	–	$\frac{\sum_{l=1}^{N_{solu}} c_l \sum_{m=1}^{N_{solv}} x_m' M_m + \rho - \sum_{l=1}^{N_{solu}} c_l M_l}{\rho_\circ} y_i^*$
	f_i^*	$\frac{\sum_{m=1}^{N_{solv}} x_m M_m}{\sum_{m=1}^{N_{solv}} x_m' M_m} f_i^*$	$\frac{\rho_\circ}{\rho}\frac{\sum_{j=1}^{N_{spec}} x_j M_j}{\sum_{m=1}^{N_{solv}} x_m' M_m} f_i^*$	–

In this table $\rho_\circ$ is the density of the solvent.

2.2.4 Osmotic and Mean Ionic Activity Coefficients

In this section two important new properties from the thermodynamics of electrolyte solutions are introduced.

2.2.4.1 Mean Ionic Activity Coefficients

As previously mentioned in this work, the chemical potential of a species j is defined according to equation 2.5. Physically, however, the indicated derivative cannot be performed for an ion, since it is not feasible to add to the solution one kind of an ion only. The majority of the published data on solute activity coefficients in electrolyte systems are, in fact, electrolyte mean ionic molal activity coefficients and not single ion ones. Researchers have attempted to do it, but only very recently reliable experimental ion activity coefficients were obtained (Khoshkbarchi and Vera, 1996a,b).

Let us consider an electrolyte with a general formula $M_{\nu+}X_{\nu-}$ that completely dissociates, according to equation 2.20, into ν_+ cations M^{z+} with charge z_+ and ν_- anions X^{z-} with charge z_-, where ν_+ and ν_- are the stoichiometric coefficients.

$$M_{\nu+}X_{\nu-} \leftrightarrow \nu_+ M^{z+} + \nu_- X^{z-} \tag{2.20}$$

The electrolyte chemical potential can be written by

$$\mu_{M_{\nu+}X_{\nu-}} = \nu_+ \mu_{M^{z+}} + \nu_- \mu_{X^{z-}} \tag{2.21}$$

Using molality scale, and choosing a standard state in the Henry's ideal solution sense, combining equations 2.11 and 2.13 for each ion and introducing in equation 2.21,

$$\mu_{M_{\nu+}X_{\nu-}} = \mu^{\bullet}_{M_{\nu+}X_{\nu-}} + \nu_+ RT \ln(m_+ \gamma^*_+) + \nu_- RT \ln(m_- \gamma^*_-) \tag{2.22}$$

where

$$\mu^{\bullet}_{M_{\nu+}X_{\nu-}} = \nu_+ \mu^{\bullet}_{M^{z+}} + \nu_- \mu^{\bullet}_{X^{z-}} \tag{2.23}$$

The molal ionic concentrations are simply related to the electrolyte molality (m) as a whole by

$$m_i = \nu_i m \tag{2.24}$$

Applying this result to equation 2.22, after some algebraic manipulations it is possible to obtain,

$$\mu_{M_{\nu+}X_{\nu-}} = \mu^{\bullet}_{M_{\nu+}X_{\nu-}} + RT\ln\left[\nu_+^{\nu_+}\nu_-^{\nu_-}m^{\nu}\left(\gamma_+^*\right)^{\nu_+}\left(\gamma_-^*\right)^{\nu_-}\right] \tag{2.25}$$

Defining the mean ionic molality, $m_{\pm}$, and the mean ionic molal activity coefficient, $\gamma_{\pm}^*$ by

$$m_{\pm} = \left(\nu_+^{\nu_+}\nu_-^{\nu_-}m^{\nu}\right)^{1/\nu} \tag{2.26}$$

$$\gamma_{\pm}^* = \left[\left(\gamma_+^*\right)^{\nu_+}\left(\gamma_-^*\right)^{\nu_-}\right]^{1/\nu} \tag{2.27}$$

it is, finally, possible to write:

$$\mu_{M_{\nu+}X_{\nu-}} = \mu^{\bullet}_{M_{\nu+}X_{\nu-}} + \nu RT\ln\left(m_{\pm}\gamma_{\pm}^*\right) \tag{2.28}$$

being ν the sum of the anion and cation stoichiometric coefficients. Although the molality was chosen here, similar equations with the same numerical quantities apply to other concentration scales.

2.2.4.2 Osmotic Coefficients

Due to the long range electrostatic forces, the deviations from ideality, in dilute electrolyte solutions, are far more pronounced than in non-electrolyte solutions. Nevertheless, the solvent activities or activity coefficients are really close to the unity, which are not adequate for calculations and fail to emphasize the departure from ideality indicated by the mean ionic molal activity coefficient.

In order to be able to use those solvent activities in an informative way, the osmotic coefficients are preferred. The practical or molal osmotic coefficient (ϕ) is defined according to:

$$\phi = -\frac{\ln\left(x_m f_m\right)}{M_m\sum_{i=1}^{N_{solu}} m_i} \tag{2.29}$$

The rational osmotic coefficient ϕ_x, based on the mole fraction concentration scale is:

$$\phi_x = -\frac{\ln(x_m f_m)}{\ln\left(1 + M_m \sum_{i=1}^{N_{solu}} m_i\right)} \tag{2.30}$$

The osmotic coefficients have the limiting value of unity at infinite dilution.

An example showing the importance of this property in electrolyte solutions can really be observed in Figure 2.3. The change of the water activity as a function of the salt molality is much less pronounced than for the osmotic coefficient: at a molality of 0.002 these values are 0.99993 and 0.98402, respectively, indicating the later a better representation of the non-ideality. This deviation from ideality, can also be seen from the molal activity coefficients presented in the same figure.

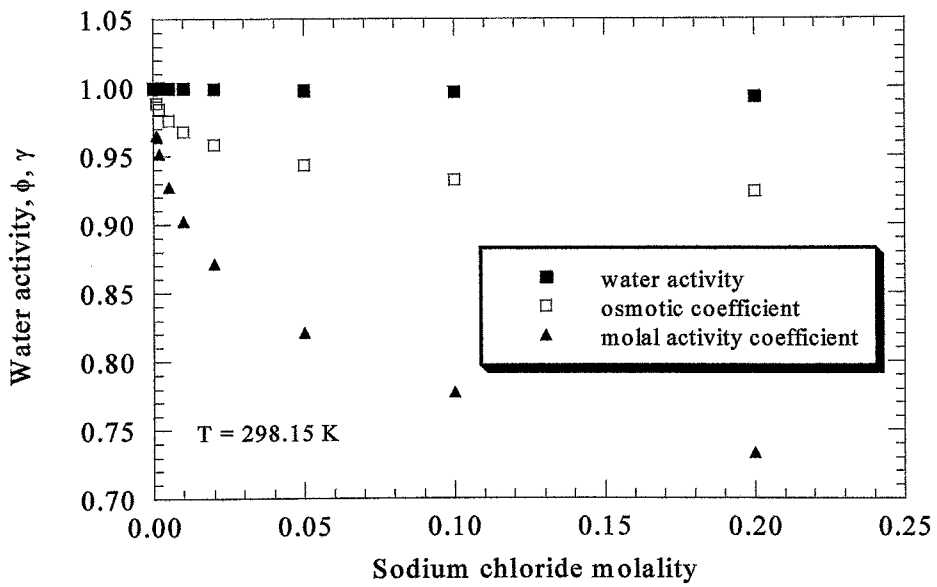

Figure 2.3 *Water activity, osmotic and molal activity coefficients of dilute NaCl in water (Clarke and Glew, 1985).*

2.2.4.3 Relation Between Osmotic and Mean Ionic Activity Coefficients

The mean ionic molal activity coefficients are, for binary solutions, frequently determined by the solvent activity measurement. The most applied experimental method is the so-called isopiestic method (Thiessen and Wilson, 1987; Pitzer, 1991; Lin et al., 1996), which is based on the principle that two solutions of non-volatile solutes distil from one to the other until their concentrations are such that the solutions have equal vapour pressure. Thus, an equation relating solvent activities (or osmotic coefficients) with the electrolyte activity coefficient should be known.

At constant temperature and pressure, the Gibbs-Duhem equation for a binary solvent/solute solution is

$$x_m d\mu_m + x_{MX} d\mu_{MX} = 0 \tag{2.31}$$

Rewriting (2.31) in the form

$$d\mu_m = -\frac{x_{MX}}{x_m} d\mu_{MX} = -\frac{m_{MX}}{1/M_m} d\mu_{MX} \tag{2.32}$$

Applying equations 2.8 and 2.28,

$$d\ln a_m = -M_m \nu m_{MX} d\ln\left(m_\pm \gamma_\pm^*\right) = -M_m \nu m_{MX}\left(d\ln m_\pm + d\ln \gamma_\pm^*\right) \tag{2.33}$$

From 2.29, coupled with result equation 2.24 it is possible to obtain

$$\ln a_m = -M_m \nu \phi m \tag{2.34}$$

Differentiating 2.34,

$$d\ln a_m = -M_m \nu\left(m d\phi + \phi dm\right) \tag{2.35}$$

observing that $m_{MX} = m$ and equalling both right sides of 2.33 and 2.35:

$$m\left(d\ln m_\pm + d\ln \gamma_\pm^*\right) = m d\phi + \phi dm \tag{2.36}$$

Noting that $\ln m_\pm$ and $\ln m$ differ only by a constant, then $d\ln m_\pm = d\ln m = \frac{dm}{m}$, and equation 2.36, after some rearrangement, becomes

$$d\ln \gamma_\pm^* = d\phi + \frac{\phi - 1}{m} dm \tag{2.37}$$

Integrating this last equation and, taking into consideration that when $m \to 0$, $\phi \to 1$ and $\gamma_\pm^* \to 1$, the desired relation is obtained:

$$\ln \gamma_\pm^* = \phi - 1 + \int_0^m \frac{\phi - 1}{m} dm \tag{2.38}$$

Inversely, when electrolyte activity coefficients are measured, by electromotive force measurements, for instance, a similar equation to obtain ϕ can be derived:

$$\phi = 1 + \frac{1}{m} \int_0^{\ln \gamma_\pm^*} m d \ln \gamma_\pm^* \tag{2.39}$$

Equations 2.38 and 2.39 have been used in the calculation of recommended osmotic and mean ionic activity coefficients for electrolytes in water.

2.2.5 Phase Equilibria Criteria

A heterogeneous closed system, at constant pressure and temperature when in equilibrium, the chemical potential of each component has the same value in all phases. In this work, two distinct phase equilibria cases are considered; vapour-liquid equilibrium and solid-liquid equilibrium (SLE).

Vapour-liquid equilibrium

Assuming an ideal vapour phase and neglecting the Poynting correction, good approximations at low pressures, the relation for phase equilibrium can be written as,

$$y_m P = x_m f_m P_m^{sat} \tag{2.40}$$

where y_m is the vapour phase mole fraction of solvent m and P_m^{sat} is the vapour pressure of the pure solvent. Since only solutions with non-volatile electrolytes will be considered, for each ion $y_i = 0$.

Solid-liquid equilibrium

The SLE criterion states that the salt chemical potential in the solid phase is equal to the sum of the constituent chemical potentials. Using equation 2.28 is then possible to write

$$\mu_{M_{\nu+}X_{\nu-}}(s) = \mu^{\bullet}_{M_{\nu+}X_{\nu-}}(l) + \nu RT \ln\left(m_\pm \gamma_\pm^*\right) \tag{2.41}$$

If the solid phase is considered to be pure salt, then its chemical potential is the same as the standard chemical potential in the solid phase: $\mu_{M_{\nu+}X_{\nu-}}(s) = \mu^{\bullet}_{M_{\nu+}X_{\nu-}}(s)$ and the equilibrium condition 2.41 may be expressed by:

$$K_{M_{\nu+}X_{\nu-}} = \exp\left(\frac{\mu^{\bullet}_{M_{\nu+}X_{\nu-}}(s) - \mu^{\bullet}_{M_{\nu+}X_{\nu-}}(l)}{RT}\right) = \left(m_{\pm}\gamma^{*}_{\pm}\right)^{\nu} \tag{2.42}$$

where $K_{M_{\nu+}X_{\nu-}}$ is defined as the solubility product of the salt.

From the fundamental equations 2.40 and 2.42 it is evident that for VLE and SLE calculations an activity coefficient model is needed. However, a considerable difference arises for the SLE problem since $K_{M_{\nu+}X_{\nu-}}$ should also be known.

For aqueous systems, eq. 2.42 has been widely used; $K_{M_{\nu+}X_{\nu-}}$ depends on the temperature and pressure and its calculation can be easily performed using the standard thermodynamic properties reported by the National Bureau of Standards (Nicolaisen et al., 1993).

Concerning mixed solvents systems, $K_{M_{\nu+}X_{\nu-}}$ also depends on the solvent composition because of the salt standard chemical potential in the liquid phase. Unfortunately, no suitable models for $\mu^{\bullet}_{M_{\nu+}X_{\nu-}}(l)$ exist yet, and to overcome this problem a new formulation is presented later in this work.

2.2.6 Excess Gibbs Energy

An excess property is defined as the difference between the actual property of the solution and that of an ideal solution at the same temperature, pressure and composition. The excess Gibbs energy (G^E) is thus defined by:

$$G^E = G - G^{ideal} \tag{2.43}$$

By partial differentiation with respect to the number of moles of component j and definition 2.5:

$$\left(\frac{\partial G^E}{\partial n_j}\right)_{T,P,n_{k\neq j}} = \mu_j^E = \mu_j - \mu_j^{ideal} \tag{2.44}$$

Using rational activity coefficients and mole fraction concentration scale to express the activity in equation 2.7, $\mu_j = \mu_j^{ref} + RT\ln(f_j x_j)$. Remembering that for an ideal solution the activity coefficient of a species j is equal to one and its chemical potential is given by $\mu_j^{ideal} = \mu_j^{ref} + RT\ln x_j$, after some rearrangements, equation 2.44 becomes:

$$\ln f_j = \frac{1}{RT}\left(\frac{\partial G^E}{\partial n_j}\right)_{T,P,n_{k\neq j}} \tag{2.45}$$

Thus, to obtain the activity coefficients, an expression for the excess Gibbs energy should be known and some of the most important G^E models are discussed in the next section. Before that, it is important to mention that equation 2.45 reflects the choices for the activity coefficients and concentration scale adopted, and to properly obtain the activity coefficients from a G^E model, it must be completely specified in that matter.

2.3 Activity Coefficients Models

Thermodynamic modelling of aqueous and mixed solvents strong electrolyte solutions has, during the last three decades, being a major area of research. Thus, in this section a general overview of some of the activity coefficient methods that have been suggested is given.

Despite the enormous amount of work that has been carried out in this area, only the most widely used and recent models or theories are presented in order to establish an understanding of the fundamental ideas beyond them. For further details the revision papers by Maurer (1983) and Renon (1986), and the books by Zemaitis et al. (1986), Pitzer (1991), Barthel et al. (1998) and Prausnitz et al. (1998) should be consulted.

The intention is not to provide an exhaustive list of models, but to give some indications about the correlation or prediction capabilities of each, concerning different kind of thermodynamic properties or equilibria. Some comparisons between them are also reported.

Initially, the most successful theoretical based theory introduced by Peter Debye and Erich Hückel is succinctly discussed together with extensions. After, the Pitzer's model is briefly reviewed due to its importance in electrolyte thermodynamics. A different kind of models, that for the first time take into account the solvent short-range forces are introduced via the

semi-empirical models. It should be mentioned that these are still a challenge in this research area. Finally, a short reference to other methods is reported, and some conclusions are drawn.

2.3.1 The Debye-Hückel Theory and Empirical Extensions

For non-electrolyte solutions short-range forces are dominant, while for solutions with electrolytes long-range electrostatic forces are very important. These forces vary inversely with the first power of the distance between ions. For other intermolecular forces, these depend on higher powers of the reciprocal distance.

Thus, even in dilute solutions, electrostatic repulsive and attractive forces between ions are significant; in the neighbourhood of a negative ion, the local concentration of positive ions is slightly higher than for the bulk solution. Thus, the attraction between the cation and the anion decreases due to the shielding effect, conditioning the distribution function of ions, which is not random even at considerable distances (Prausnitz et al., 1998).

If the distribution is known, it is possible to calculate the electrical potential, which in turn depends on the former. To solve the problem Debye and Hückel (1923) combined the Poisson equation of electrostatic theory with the Boltzmann distribution law, being able to calculate the electrical potential at any point of the solution in terms of the concentration and charges of the ions and properties of the solvent.

Working this result for the electrical potential through well-established concepts from classical electrostatics, a simple expression for the unsymmetric rational activity coefficient of an ion, in a dilute solution, was derived. The original results, presented for instance by Robinson and Stokes (1970), were obtained in terms of the molar concentration scale. However, in order to use it in a practical way it is common to write that expression in accordance to:

$$\ln f_i^* = -Az_i^2 \frac{\sqrt{I}}{1 + Ba\sqrt{I}} \tag{2.46}$$

where I is the so-called molal ionic strength defined as:

$$I = 0.5 \sum_{i=1}^{N_{solu}} m_i z_i^2 \tag{2.47}$$

and z_i is the ion charge number, a is the so-called distance of closest approach between ions, in meters, and the temperature dependent constants A and B are given by:

$$A = \frac{\sqrt{2*1000N_A}}{8\pi}\left(\frac{e^2}{\varepsilon_\circ k}\right)^{1.5}\frac{\rho_\circ^{0.5}}{(\varepsilon T)^{1.5}} = 4.20416*10^6\frac{\rho_\circ^{0.5}}{(\varepsilon T)^{1.5}}\ kg^{0.5}mol^{-0.5} \qquad (2.48)$$

$$B = \sqrt{2*1000N_A}\left(\frac{e^2}{\varepsilon_\circ k}\right)^{0.5}\left(\frac{\rho_\circ}{\varepsilon T}\right)^{0.5} = 5.03045*10^{11}\left(\frac{\rho_\circ}{\varepsilon T}\right)^{0.5}\ kg^{0.5}mol^{-0.5}m^{-1} \qquad (2.49)$$

In these equations ε is the solvent dielectric constant. All the other relevant constants are:

$N_A \equiv$ Avogrado's number $= 6.02380*10^{23}\ mol^{-1}$

$e \equiv$ electronic charge $= 1.60218*10^{-19}\ C$

$\varepsilon_\circ \equiv$ vacuum permittivity $= 8.85419*10^{-12}\ C^2J^{-1}m^{-1}$

$k \equiv$ Boltzmann constant $= 1.38026*10^{-23}\ JK^{-1}$

The Debye-Hückel (DH) equation (2.46) gives the activity coefficient for the ions, not for electrolytes in electrically neutral solution. Applying the DH equation into equation 2.27, taking into consideration that the individual activity coefficients do not depend on the nature of the ion, but only on their concentration and charge, the mean ionic rational activity coefficient ($f_\pm^*$) is

$$\ln f_\pm^* = -\frac{A|z_+z_-|\sqrt{I}}{1+Ba\sqrt{I}} \qquad (2.50)$$

At infinite dilution, $I \to 0$ and the DH equation reduces to the well-known Debye-Hückel limiting law (DHLL)

$$\ln f_\pm^* = -A|z_+z_-|\sqrt{I} \qquad (2.51)$$

This last equation result does not include any adjustable parameter and may be considered an exact theory for very dilute electrolyte solutions. It was proved to be suitable to ionic strengths up to 0.001 mol/kg.

In their original work Debye and Hückel (1923) showed that if the parameter a, in equation 2.50, was considered an adjustable parameter the validity of the model could be extended to ionic strengths 10 times higher than for the DHLL.

Some further refinements were introduced in the DH equation by Güntelberg in 1926 and by Guggenheim in 1935 (Zemaitis et al., 1986). Güntelberg suggested that a fixed value of 3.04 Å for the distance of the closest approach (a) of ions in water at 298.15 K gives results comparable to those obtained when the parameter is adjusted from experimental data. Introducing this, the resulting expression is:

$$\ln f_{\pm}^{*} = -\frac{A|z_{+}z_{-}|\sqrt{I}}{1+\sqrt{I}} \tag{2.52}$$

Guggenheim added a new salt specific electrolyte interaction parameter ($b_{\pm}$). The equation is an extension of the Güntelberg expression,

$$\ln f_{\pm}^{*} = -\frac{A|z_{+}z_{-}|\sqrt{I}}{1+\sqrt{I}} + b_{\pm}I \tag{2.53}$$

This equation is limited to one electrolyte in solution, but is especially effective for strong electrolytes, with unity charge for both ions in water. For this case, it gives a good representation for ionic strengths up to 1 mol/kg. Usually the range of applicability of this model is limited to ionic strengths up to 0.1 mol/kg.

Matching the original derivation, in this work, equations 2.50 to 2.53 are all written in terms of mean ionic rational activity coefficient. However, it is usual to find them written in terms of the mean ionic molal activity coefficient ($\gamma_{\pm}^{*}$), like in the book by Zemaitis et al. (1986). At this point it should be stressed out that confusion usually arising from that fact could be avoided, by indicating that the conversion factor between them at very low molalities is around 1 (see Table 2.2), which is not the case when they are used at higher molalities like for the Guggenheim equation.

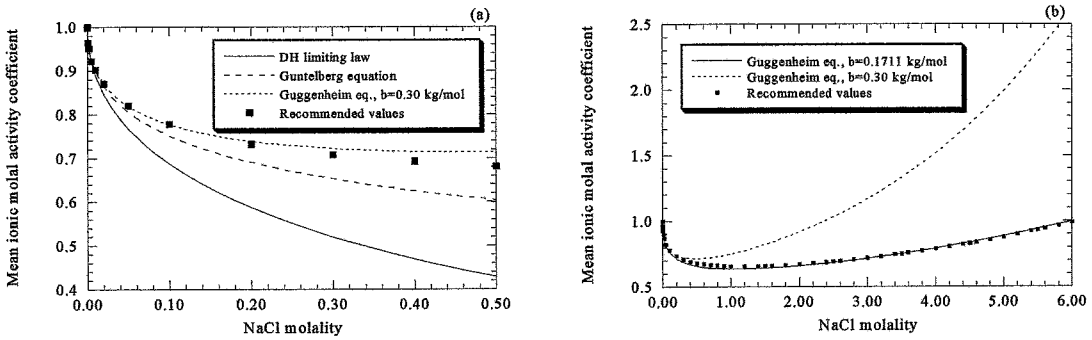

Figure 2.4 *Mean molal activity coefficients of NaCl in water at 298.15 K: (a) Comparison between DHLL, Güntelberg and Guggenheim equations, (b) Guggenheim equation with different values for the parameter $b_{\pm}$. Recommended values by Clarke and Glew (1985).*

Figure 2.4a shows a comparison between the recommended values, based on an extensive experimental database for activity coefficients of NaCl aqueous solutions at 298.15K, given by Clarke and Glew (1985) for the Dow Chemical Canada Inc., with those calculated from equations 2.50, 2.52 and 2.53, taking $A = 1.1744\ kg^{0.5}mol^{-0.5}$ ($\rho_{\circ} = 0.997\ kgdm^{-3}$; $\varepsilon = 78.41$). It should be mentioned that for the calculations with the DHLL and Güntelberg equation the conversion between the rational and the molal activity coefficients was made. For the Guggenheim equation, as the parameter $b_{\pm} = 0.30\,kgmol^{-1}$ was taken from Zemaitis et al. (1986), no correction was done. Figure 2.4b presents calculations with the Guggenheim equation in the original form (2.53), with a parameter value estimated in this work using the same recommended values ($b_{\pm} = 0.1711\,kgmol^{-1}$), and that suggested by Zemaitis et al. (1986).

The main assumption in the Debye-Hückel theory is to consider that deviations from ideality are only due to electrostatic forces between the ions, which is physically reasonable at high dilution but unreal when the ionic concentration rises and short-range forces become dominant. Guggenheim suggested the use of power series in electrolyte concentration to better describe the physical chemistry of electrolyte solutions, leading to the virial expansion models.

The Bromley's model (Bromley, 1972), one of the proposed virial expansions, introduced big improvements to Guggenheim's equation without any additional parameter. An empirical expression for the parameter $b_{\pm}$ as a function of I was proposed for more than 100 aqueous salt systems at 25 °C, extending the ability to correlate the activity and osmotic coefficients to ionic strengths up to 6 molal.

Later developments included an empirical (5 parameter) expression for the temperature dependency on $b_{\pm}$ (Bromley, 1973) and an extension to multi-ion solutions (Bromley et al., 1974).

The most applied virial expansion model is due to Pitzer and co-workers and is briefly discussed in the coming section.

2.3.2 Pitzer's Model

Since 1973 the model by Pitzer has been widely used to describe thermodynamic properties of aqueous electrolyte solutions for systems of interest for the chemical industry. It is an extension of the Guggenheim-Scatchard proposals, using virial coefficients to represent binary and ternary short-range interactions between ions.

According to Pitzer (1973) the unsymmetric excess Gibbs energy ($G^{E,*}$) for an electrolyte in a solvent m is given by

$$\frac{G^{E,*}}{RTn_m M_m} = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) + \sum_i \sum_j \sum_k m_i m_j m_k \Lambda_{ijk} + \cdots \qquad (2.54)$$

This general equation may be considered as the sum of two main kind of interaction forces; the long-range interaction forces expressed by the function $f(I)$, which is a modified Debye-Hückel term, and the ionic short-range interaction forces described by a virial expansion on the molality truncated after the third term as indicated by the summations. The parameters λ_{ij} and Λ_{ijk} are a measure of the binary and ternary interactions between ions, respectively.

Though the model presents a theorethical basis, the final expression is, at least, partly empirical since the functions on ionic strength $f(I)$ and $\lambda_{ij}(I)$ were established choosing, after data correlation, the best fit. The final equations, derived from 2.54, for the mean ionic molal activity coefficients, as well as for the osmotic coefficients are presented elsewhere (Pitzer, 1973; Pitzer and Mayorga, 1973; Pitzer and Kim, 1974; Pitzer, 1991).

For an electrolyte constituted by, at least, one univalent ion, in aqueous solution at 25 °C, Pitzer and Mayorga (1973) presented the three salt specific correlation parameters for more than 200 electrolytes studied, in a concentration range up to 6 molal.

Extensions for higher valence type electrolytes (Pitzer and Mayorga, 1974) and mixed electrolyte solutions (Pitzer and Kim, 1974) require additional parameters to satisfactorily describe their behaviour. The re-evaluation of those parameters was carried out by Kim and Frederick (1988a,b) enlarging the molality range of applicability.

Studies were performed afterwards for weak electrolyte systems, in the very important H_2SO_4/water system (Pitzer et al., 1977). Furthermore, it turned out that if other thermodynamic properties like enthalpy and heat capacity were considered or the temperature range became broader, the introduction of temperature dependency, for the three specific salt parameters, was inevitable. The extreme difficulty to rigorously describe the thermodynamic properties of electrolyte systems is totally shown by the need of 19 parameters for an accurate description of NaCl/water system behaviour in a temperature range between 0 to 300 °C and a maximum molality of 10.4 molal (Silvester and Pitzer, 1977).

Despite the somewhat high number of regressed parameters for large temperature and pressure ranges, the Pitzer's model has still been, very useful and extremely used in the calculation of thermodynamic properties of one salt or multisalt aqueous solutions (Rard and Archer, 1995; Archer and Rard, 1998; Holmes and Mesmer, 1998).

To study high concentrated ionic systems or to use pure fused salt as standard state for electrolytes, the model of Pitzer is not appropriate because molality tends to infinite. To overlap this problem Pitzer and co-workers (Pitzer, 1980; Pitzer and Simonson, 1986) developed new expressions, obeying the Debye-Hückel liming law, for the ions or solvent activity coefficients, using the mole fraction concentration scale. This methodology was successfully used (Simonson and Pitzer, 1986) in the calculation of water vapour pressures over $LiNO_3/KNO_3/H_2O$ solutions at high temperatures and concentrations (maximum molality 55.5 mol/kg).

For non-aqueous solvents the model has been rarely used and for mixed solvent systems even less. In fact, the Pitzer's model does not take into consideration the ion-solvent and solvent-solvent short-range interaction forces, which are very important in these systems. Koh et al. (1985) and González-Diaz et al. (1995), among others, used the Pitzer equations to calculate mean ionic molal activity coefficients of salts in mixed solvents from electromotive force measurements data, employing two parameters for each solvent composition. Even if the results may be considered good, the parameters have high uncertainty and the model is not practical for further use.

The short-range forces gain importance as far as the electrolyte concentration rises. The model of Pitzer does not take, however, them properly and extension to mixed solvent systems would require further parameters as a function of solvent composition, and no theoretical basis for those functions are known. To better describe solvent-solvent and solvent-ion interaction forces, models from non-electrolyte thermodynamics were introduced giving birth to the so-called semi-empirical models.

2.3.3 Semi-Empirical Models

In the semi-empirical models it is usual to assume the total unsymmetric excess Gibbs energy of an electrolyte solution (or equivalently, the dimensionless excess Gibbs energy, $G^{E,*}/RT$) as the sum of two independent contributions; one arising from the long-range forces (LR) and the other from the short-range ones (SR):

$$\frac{G^{E,*}}{RT} = \frac{G^{E,*}_{LR}}{RT} + \frac{G^{E,*}_{SR}}{RT} \tag{2.55}$$

While for the LR forces a Debye-Hückel type term is often used, several choices are possible for the SR forces representation. Among those, the most commonly used are the local composition models NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975).

2.3.3.1 NRTL Based Models

The first work published on electrolyte solutions using the NRTL model was by Cruz and Renon (1978). It was used for the correlation of mean ionic molal activity and osmotic coefficients in binary aqueous solutions of partially or completely dissociated electrolytes at 298.15 K. Additionally to the terms included in equation 2.55, another contribution, the so-called Debye-McAulay contribution, to correct the change on the medium dielectric constant produced by the increase of the electrolyte concentration, containing two adjustable parameters for each binary salt system, was introduced. In order to reduce the total number of fitted parameters, this model takes the ion pairs as if they are undissociated molecules, and the free ions are assumed to be mainly surrounded by solvent molecules. Formally, these assumptions for the structure of the solution lead to the fitting of two interaction salt-solvent interaction parameters, for total dissociation, able to represent quite concentrated aqueous electrolyte solutions.

Ball et al. (1985) proposed a modified Cruz and Renon model by simplifying the Debye-McAulay contribution. Instead of considering a two-parameter correlation for the change on the dielectric constant, in this approach that was calculated using an expression based on the ionic radii. Thus, only two parameters are left to correlate the osmotic coefficients of pure aqueous electrolytes at 298.15 K up to 6 molal.

The model proposed by Chen and collaborators (Chen et al., 1982; Chen and Evans, 1986) is an appealing NRTL based model for electrolyte solutions. For the long-range contribution an extended form of the Debye-Hückel equation proposed by Pitzer (1980) is used, the Pitzer-Debye-Hückel equation. The local composition NRTL equation developed is based on two fundamental assumptions about the fluid lattice structure of electrolyte systems:

> *Like-ion repulsion*: the local composition of cations around cations is zero (and likewise for anions around anions). This means that the repulsive forces between like charged ions are very large.
>
> *Local electroneutrality*: the local distribution of cations and anions around a central molecule is such that the net local ionic charge is zero.

The two binary interaction parameter model was used to correlated electrolyte mean ionic molal activity coefficients for more than 100 aqueous binary systems at 298.15K up to 6 molal, and was after generalized to multicomponent electrolyte aqueous systems using only binary parameters (Chen and Evans, 1986). Chen (1986) has also performed solubility calculations for binary and ternary aqueous electrolyte systems.

Table 2.3 shows a comparison between the Pitzer, the modified Cruz and Renon, and the Chen models concerning the osmotic coefficients representation in aqueous electrolyte solutions at 298.15 K. All these models involve a two parameter correlation for solutions with one salt. To test the models prediction capabilities, the parameters fitted to salt/water solutions were used to calculate the osmotic coefficients of aqueous mixtures of two salts (Ball et al., 1985).

Table 2.3 Comparison between different models concerning the correlation or prediction of osmotic coefficients in aqueous electrolyte solutions.

Systems Type		Root Mean Square Deviation (%) for ϕ		
Salt	Number	Pitzer	Ball et al. (1985)	Chen and Evans (1982)
Uni-univalent	27	0.5	0.6	0.9
Other Salts	13	1.8	2.4	5.5
Two Salts*	21	1.4	1.9	1.8

*Predictions.

To extend the aqueous electrolyte NRTL model in order to represent the phase equilibrium of mixed solvent electrolyte systems, specifically regarding VLE, a major modification was introduced. The long-range interaction contribution of the Pitzer-Debye-Hückel expression, although essential in computing electrolyte activity coefficient, was found to have little effect on the phase equilibrium behaviour of the solvent. Therefore, that contribution was dropped out and only the local interaction term of the electrolyte NRTL model was used (Mock et al., 1986).

The correlation of VLE for a two-solvents/one salt system requires 9 parameters, but only three obtained from the ternary mixed solvent/salt experimental data. However, the main disadvantage of the model is that different parameters are required to calculate VLE at different temperatures or pressures, not allowing any predictions.

Some other different approaches using the NRTL model worth to mention are from Tan (1990) and Kolker and de Pablo (1995a,b; 1996a,b).

After a series of publications dealing with the Wilson equation (Wilson, 1964) for electrolyte systems (Tan, 1987; Tan and Ti, 1989), Tan (1990) developed a model for the representation of VLE in mixed solvent systems with undissociated solute, only involving short-range forces. The model is an extension of the original NRTL equation considering a contribution to the excess Gibbs energy of mixing using local mole fraction of the dissolved solute solvated in the environment of each solvent component. The parameters between the solvent components are regressed from isobaric VLE data for the mixed solvent, while those between the solute and each solvent are computed from bubble point data for the binary system at the same solute concentration and pressure of the ternary mixture.

Thus, only with solute free mixed solvent isobaric VLE data and two experimental determinations of the bubble points of each solvent, at a given solute concentration and pressure, it is possible to predict the VLE of solute/mixed solvent systems. The study was carried out for 75 solute-solvents systems and the model was found to give good predictions for the vapour composition and bubble point for a given liquid composition. Later developments of these studies were done in order to predict the mixed salt effects on mixed solvent VLE (Tan and Ng, 1993).

Figure 2.5 shows the vapour composition and boiling temperature predicted curves with Tan's model for a one molal solution of KCl in methanol/water mixed solvent system at 760 mmHg, and the equivalent experimental values (Boone et al., 1976). The calculations were performed using the parameters listed by Tan (1990).

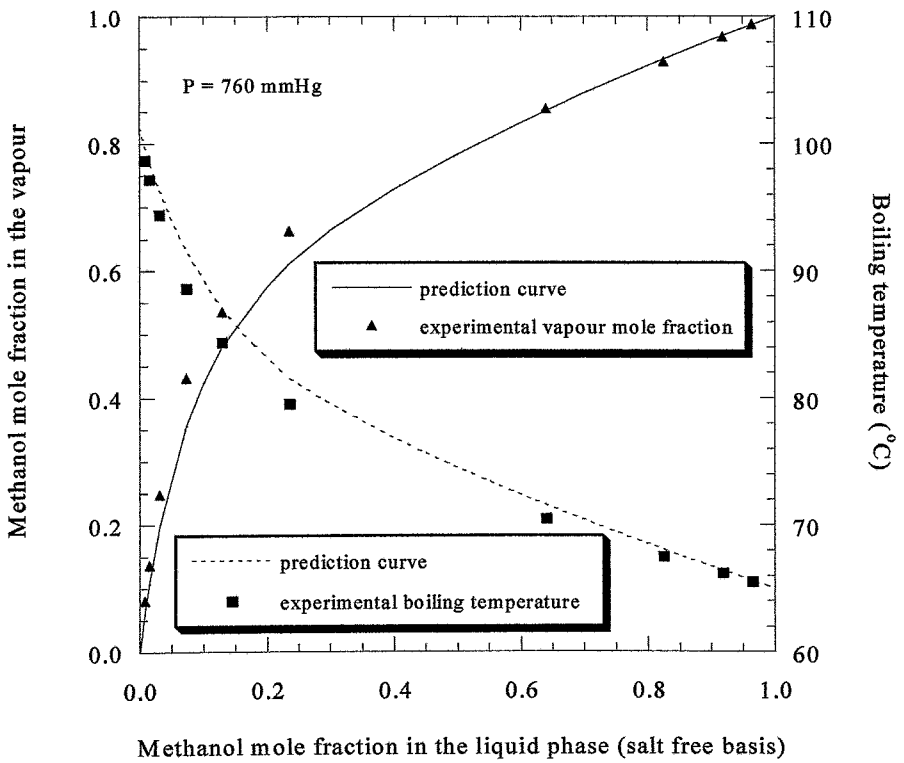

Figure 2.5 *Comparison between experimental (Boone et al., 1976) and the predicted curves with Tan's model, for the vapour composition and boiling temperature in the 1 molal methanol/water/KCl system.*

Kolker and de Pablo (1995a,b) developed a NRTL based method, that does not require any estimated parameters from the ternary data, for the calculation of activity coefficients in multicomponent aqueous systems. It was applied for the representation of the solubility of salts or gases and water activity.

After this, the method was extended to water/alcohol mixed solvent systems (Kolker and de Pablo, 1996a,b). The expressions for the activity coefficients were derived by integrating the Gibbs-Duhem equation for multicomponent systems. To predict VLE and SLE it is only necessary to know pure component and infinite dilution data for the solute and solvents. The model can predict quantitatively the salt effect in VLE, but for SLE calculations only reasonable agreement is achieved. Furthermore, the accuracy of the predictions varies considerably from one system to another, and the effect of the temperature on the solubilities is not considered.

2.3.3.2 UNIQUAC Based Models

The application of the UNIQUAC model for electrolyte systems was first developed by Christensen et al. (1983), but only during 1986 the main results attained for VLE in water/alcohol/salt systems were reported (Sander et al., 1986). The model includes a long-range contribution, given by the Debye-Hückel expression, and a short-range one, accounted by the modified UNIQUAC model with concentration dependency on the interaction parameters.

Sander et al. (1986) had some difficulties to apply the Debye-Hückel expression to mixed solvent systems. It was necessary to fix A and B parameters, without considering their variation due to the change on the dielectric or density of the mixed solvent, to avoid systematic erroneous conclusions. Cardoso and O'Connell (1987) solved this problem deriving rigorous expressions for the activity coefficients, due to long-range forces, in multisalt-multisolvent mixtures.

To correct the representation of long-range forces in the Sander's model, Macedo et al. (1990) properly modified the Debye-Hückel term and extended the database used by Sander et al. (1986), publishing a new parameter table. The results are pretty close, but the later model has a correct theoretical foundation. This last version of Sander's model has been widely used for the correlation and/or prediction of VLE in mixed solvent systems. Figure 2.6 shows the composition-composition diagram predicted with the modified UNIQUAC model (Macedo et al., 1990) compared to the experimental data obtained by Iliuta et al. (1996). As can be observed the prediction is very satisfactory.

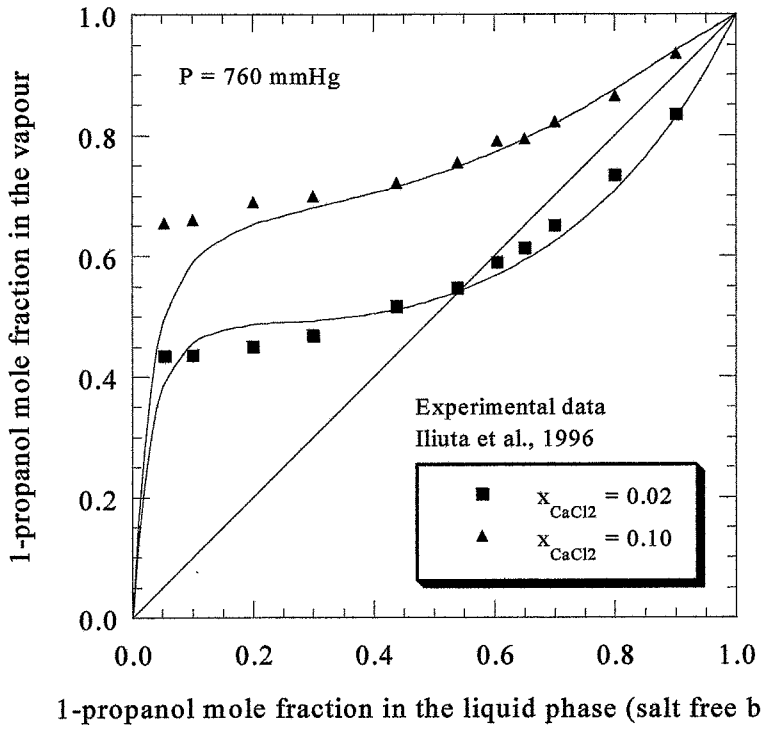

Figure 2.6 *Vapour-liquid equilibrium diagram for the system 1-propanol/water/$CaCl_2$ at two different salt concentrations. Prediction curves by the modified UNIQUAC.*

Some other modifications of the extended UNIQUAC model for electrolytes have been successfully employed to correlate and predict the solubilities of salts in aqueous systems (Nicolaisen et al., 1993; Nicolaisen, 1994; Thomsen, 1997; Thomsen et al., 1998).

Besides the short and long-range contribution forces set in equation 2.55, Li et al. (1994) added a middle-range (MR) interaction contribution, since the indirect effects of the presence of charges, like charge-dipole and charge-induced dipole interactions, should be, in the opinion of the authors, reflected in the model. This term, derived from statistical thermodynamics, introduces new parameters to correlate, but the concentration dependency on the UNIQUAC equation, used in the above-mentioned models has been dropped out. Concerning the long-range forces the same equations are used.

This model is used for VLE, osmotic and mean ionic molal activity coefficients calculations up to 26 molal (Polka et al., 1994). In Table 2.4 a comparison between this model and the one by Macedo et al. (1990) is outlined, concerning vapour pressures in salt/water systems and isobaric VLE in mixed solvents.

Table 2.4 Comparison between two different UNIQUAC based models.

	Water-Salt Systems			Mixed Solvent Systems			
Model	Data Sets	Parameters	ΔP (%)	Data Sets	Parameters	ΔY (%)	ΔT (%)
Macedo et al.	41	7	2.9	116	14	5.0	1.8
Li et al.	41	12	1.5	116	22	3.2	1.4

Although the model by Li et al. (1994) gives better accuracy than the model by Macedo et al. (1990), it involves a much higher number of fitted parameters, both for binary and ternary systems. Therefore, the small difference between their performances does not advise the use of the Li et al. (1994) model.

2.3.3.3 UNIFAC Based Models

Despite its importance for non-electrolyte systems, the UNIFAC group-contribution model (Fredenslund et al., 1977) has not been used as much as expected to describe the short-range forces in electrolyte systems.

Following the ideas by Macedo et al. (1990), in the model suggested by Kikic et al. (1991) the UNIQUAC equation was substituted by the original UNIFAC method with the same interaction parameters between the solvent groups as in the original work (Gmheling et al., 1982). Only the interaction between ions and the solvent groups were estimated, attaining an average accuracy for the vapour phase composition lower to the UNIQUAC model. However, since it is a group-contribution method, it has a much broader range of applicability and even more, it is worthwhile mentioning that the parameters are concentration independent.

Achard et al. (1994) applied the modified UNIFAC (Larsen et al., 1987), with temperature dependent interaction parameters between solvent groups, combined with a constant solvation of each ion by water molecules. The short-range activity coefficients were corrected for the true mixture composition obtaining similar results to the previous UNIFAC model by Kikic et al. (1991).

The solvation concept in the thermodynamics of electrolytes is briefly discussed in the following section.

2.3.3.4 Solvation Models

The idea for solvation models comes from the good physicochemical evidence that in many electrolyte solutions the ion is not a free entity but has solvent molecules firmly attached. In this way, Stokes and Robinson (1973), assuming that only cations can be solvated until a fixed upper limit of water molecules is achieved, developed a model for aqueous solutions where the hydration phenomenon is treated as equilibrium of various stages of hydration. Thus, with two correlation parameters, for each salt, they were able to represent osmotic coefficients at 25 °C up to 30 molal.

More recently, Lu and Maurer (1993) used this concept together with a Pitzer-Debye-Hückel expression (Pitzer, 1973) for the long-range forces and the UNIQUAC model for the short-range ones. Admitting the hydration for cations and anions, the number of parameters increased, but the correlation results for osmotic and activity coefficients at 25 °C are very impressive.

To apply this concept to mixed solvent systems, Zerres and Prausnitz (1994) presented a semi-empirical method with a physical contribution described by a van Laar expression, a long-range term as derived by Cardoso and O'Connell (1987), and a chemical stepwise solvation process. Like Robinson and Stokes, the authors considered that only the cation is solvated until a possible fixed maximum of binding sites. The equilibrium solvation constant for each step is calculated from statistical considerations leaving only one correlating parameter. The model was developed in order to represent water/organic solvent/salt VLE using only one adjustable parameter from ternary data, and the achieved agreement is good. Unfortunately, only a few cases were studied, but the big feature of this model is that liquid-liquid equilibrium (LLE) is described simultaneously.

Ohe (1998) has recently modified his original solvation model in order to predict the salt effect in VLE for multicomponent/salt system using only the solvation number regressed from binary data. The method seems to be powerful, using only the solvation number to predict vapour compositions and bubble points in three mixed solvent systems with good accuracy.

2.3.4 Other Models

Different methods from those expressed before have been developed. Typical examples are based on the molecular simulation and equations of state. Until the ends of the eighties few attempts to use equations of state to electrolyte solutions have been reported. Nevertheless, these models fail to give the theoretically-required behaviour at dilute conditions, or were applied only to the liquid phase (Raatschen et al., 1987).

Using an equation of state developed from an expression of the Helmholtz free energy, Zuo and Fürst (1998) were able to describe mean ionic coefficients and VLE in water/alcohol systems with deviations around 0.02 for the vapour-phase composition and 3% for mean ionic molal activity coefficients. Another interesting approach is due to Dahl and Macedo (1992), who used the MHV2 equation of state for both VLE and LLE with very good results.

Application of molecular simulations to electrolyte systems has been very specific in terms of the studied systems and much has still to be done. Some examples of application to mixed solvent electrolyte systems showed that the behaviour can only be predicted qualitatively (Wu and Lee, 1992; Strauch and Cummings, 1993).

2.4 Conclusions

It is obvious that thermodynamics of electrolyte solutions is not a minor extension of non-electrolyte thermodynamics. The fundamental question about their degree of dissociation and phenomena like ion-association or solvation leave some doubts about the total number of different species in solution. It is then common to classify the electrolytes as strong, when it is assumed that they are completely dissociated into anions and cations, and weak electrolytes, when the chemical equilibrium plays an important role as it is shown in chapter 5.

As fundamental concepts, the different concentration scales used have been focused being the molality and mole fraction scales the most used. The standard sates, which usually are different for solvents and for solutes have also been analysed, leading to the unsymmetric convention where the activity coefficients of all components go to unity at infinite dilution or the symmetric convention where that value is attained in the case of pure component. Special attention has been given to the very important conversions between the several possible activity coefficients obtained for those concentration scales and standard states.

The activity coefficients of the individual ions are not measurable quantities. Thus, the definition of mean ionic activity coefficients was introduced for electrolytes. This coefficient gives real indication of the deviation from ideality even at infinite dilution, while the solvent activity does not, leading to the introduction of the osmotic coefficient concept.

In fact, even at high distances, there are strong interactions between ions. The electrostatic forces are well represented at infinite dilution through the Debye-Hückel theory. However, as the ionic concentration rises extensions of this theory are required and some examples have been presented.

Pitzer's model is the most successful model for aqueous solutions, while for mixed solvent systems several semi-empirical models have been reviewed. Absolute comparisons between them are very difficult to make because the models contain different number and type of interaction parameters that may change from system to system. However, these models correlate osmotic and mean ionic activity coefficients in aqueous systems within 1 to 2% and have the important characteristic of being easily extended to mixed solvent solutions.

A large amount of both experimental and modelling work has been carried out for VLE in mixed solvent systems. Much different is the case concerning LLE or SLE. The importance of the last in the understanding of the salt effect in VLE and the stringent test of those models in their capabilities to represent different types of equilibria lead to the establishment of a project for salt solubilities in mixed solvents. This project is presented in the next chapters.

List of Symbols

a	distance of closest approach, m
a	activity
A	constant defined according to equation 2.48, $kg^{0.5}mol^{-0.5}$
B	constant defined according to equation 2.49, $kg^{0.5}mol^{-0.5}m^{-1}$
$b_{\pm}$	parameter according to equation 2.53, $kgmol^{-1}$
c	molarity, $moldm^{-3}$
e	electronic charge, C
f	rational activity coefficient
$\hat{f}$	fugacity
$f(I)$	Debye-Hückel term in equation 2.54
G	Gibbs energy
I	ionic strength, $molkg^{-1}$
k	Boltzmann constant, JK^{-1}
K	solubility product
l	liquid state
m	molality, $molkg^{-1}$
M	molecular weight, $kgmol^{-1}$
M	cation
MX	electrolyte
n	mole number
N_A	Avogrado's number, mol^{-1}
N_{solu}	total number of solutes
N_{solv}	total number of solvents
N_{spec}	total number of species
P	pressure
R	ideal gas constant, $Jmol^{-1}K^{-1}$
s	solid state
T	absolute temperature, K
V	volume of the system, dm^3
x	mole fraction in the liquid phase
X	anion

y	mole fraction in the vapour phase
y	molar activity coefficient
z	ionic charge

Greek Letters

γ	molal activity coefficient
Δ	property difference
ε	solvent dielectric constant
$\varepsilon_\circ$	vacuum permittivity, $C^2 J^{-1} m^{-1}$
θ	concentration scale
λ	binary interaction parameter in equation 2.54
Λ	ternary interaction parameter in equation 2.54
μ	chemical potential
ν	stoichiometric coefficient of the ion
ρ	solution density, $kgdm^{-3}$
$\rho_\circ$	solvent density, $kgdm^{-3}$
ϕ	molal osmotic coefficient
ϕ_x	rational osmotic coefficient

Subscripts

i	solute or any species
j	any species
k	any species
l	solute species
LR	long range
m	solvent
MX	electrolyte
SR	short range
$+$	cation
$-$	anion
$\pm$	mean ionic property

Superscripts

E	excess property
ideal	ideal state
ref	reference state
sat	saturation
$\circ$	solvent standard state
$\bullet$	standard state
$*$	unsymmetric
∞	infinite dilution
θ	concentration scale: c molar, m molal, x mole fraction
'	solute free basis

Abbreviations

DH	Debye-Hückel
DHLL	Debye-Hückel limiting law
LLE	liquid-liquid equilibrium
LR	long-range
MR	middle range
SLE	solid-liquid equilibrium
SR	short-range
VLE	vapour-liquid equilibrium

Chapter 3

SOLID-LIQUID EQUILIBRIUM: EXPERIMENTAL STUDY

3. Solid-Liquid Equilibrium: Experimental Study

3.1 Introduction

Salt solubility plays an important role in many industrial processes. However, as pointed out in the previous chapter, attention was until nowadays much more concentrated on experimental and theorethical studies of other thermodynamic properties or phase equilibrium of the electrolyte solutions. Therefore, in this chapter a literature search in terms of the experimental available data and methods for the salt solubility measurement is initially presented, in order to establish an experimental programme and implement an accurate method to carry it out. After, details of the experimental method and the measured experimental solubilities are given as well as a critical analysis of the obtained data. Finally, some conclusions are drawn concerning this experimental study.

3.2 Literature Survey on Salt Solubility

The study of phase equilibria in electrolyte systems and more specifically the determination of salt solubilities are extremely important, either from a scientific or an industrial point of view. Besides the many relevant indications that can be given concerning the liquid phase structure and its thermodynamic properties, it is also very useful as a support for the design and simulation of unity operations such as crystallization, extractive distillation and liquid-liquid extraction (Horvath, 1985; Furter, 1992; Korin and Soifer, 1997).

In fact, the solubility of salts can give important indications about possible or probable solution structures and have been used along with appropriate classical thermodynamics theory, to deduce Gibbs energies of transfer from a reference pure solvent to mixed solvents (Emons et al., 1984; Labban and Marcus, 1991; Lorimer, 1993). On the other hand, to design processes in order to find the best operation conditions, the variables such as temperature and solvent composition should be accounted on the salt solubilities. These data together with other thermodynamic properties may be used to provide a methodology to correlate and/or predict salt solubilities.

In this way a literature survey of the available solubility data and experimental methods for its measurement was carried out in order to choose the kind of systems to be studied as well as the experimental technique to perform the measurements.

3.2.1 Salt Solubility Data

After an extensive literature search based on the compilation books by Stephen and Stephen (1963; 1964) and Linke and Seidell (1958; 1965), and the open literature, it is possible to conclude that up to now, only aqueous electrolyte systems have received the deserved attention. On the contrary, for organic solvent/salt or mixed solvent/salt systems there is a great lack of experimental information.

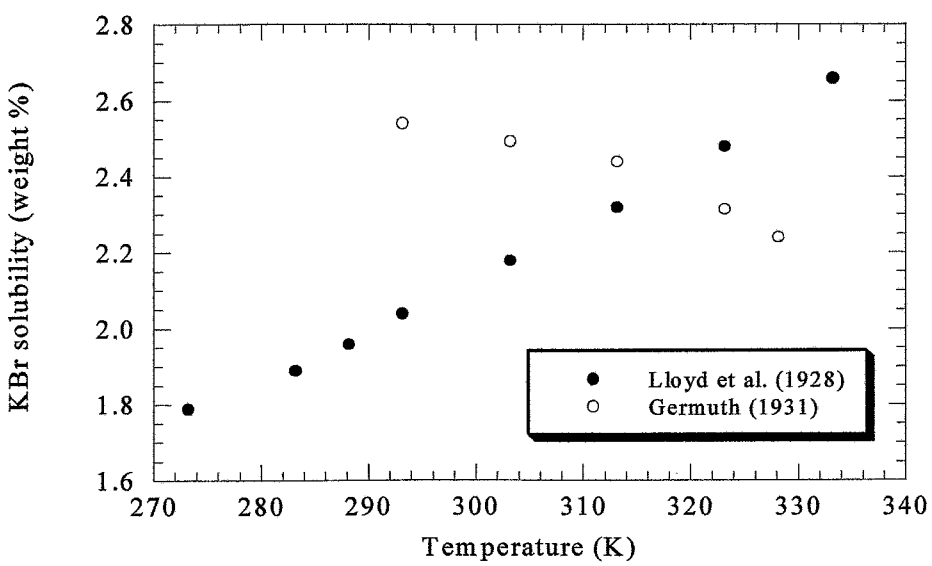

Figure 3.1 *Comparison between different literature sources for the solubility of KBr in methanol at several temperatures.*

For the binary systems it is possible to find the temperature influence on the solubility, but discrepancies like those presented in Figure 3.1 are usually detected.

Thus, if the solubility of a salt is needed, even for the most common solvents like methanol or ethanol, the most probable is not to find any reliable information, but luckily some rare comprehensive studies like the one by Stenger (1996) may be found. This author presents the solubility of several salts in methanol at 25 °C, a study for the Dow Chemical Company, and concluded that some experimental determinations should be carried out either to check some values or only because none was reported.

For mixed solvent systems the available solubility data are also very scarce and the majority is old. Most of the data are from the first half of this century leaving some doubts about their quality and the temperature influence on the solubility is almost ignored since the majority of the published data are at 298.15 K. As shown in Figure 3.2, even at this temperature, the values published by different authors may attain very large deviations among them.

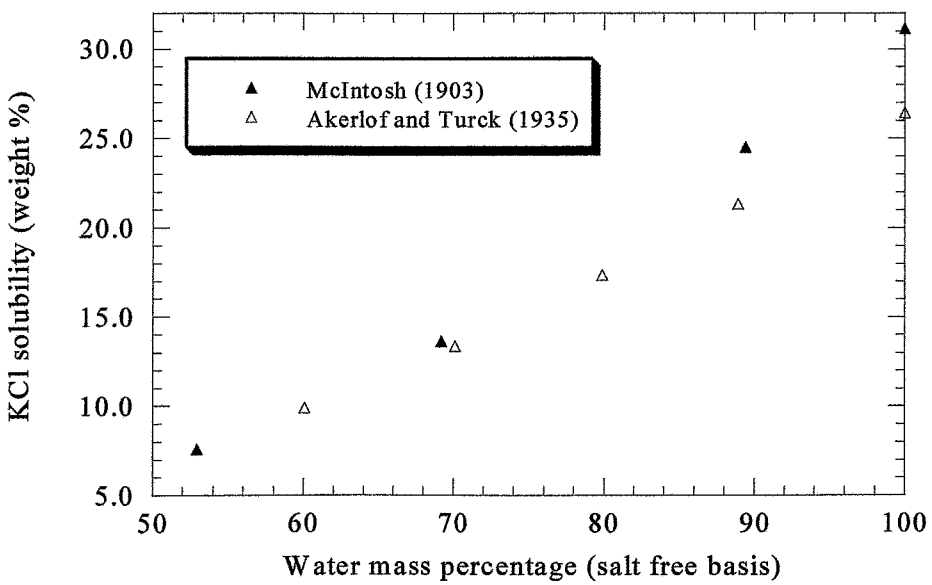

Figure 3.2 *Solubility of KCl in water/methanol solvent mixture at 298.15 K: comparison between the values reported by different authors.*

For SLE data, no thermodynamic consistency data tests are available. To check the quality of the data some procedures can be implemented. One is, for instance, a comparison between the accepted binary salt solubility values with the same reported for mixed solvent sources, or alternatively to estimate the quality of the salt solubility isotherms along the solvent composition making a curve fit with an empirical equation and analyse the deviations from

the curve. This last strategy was used by Linke and Seidell (1965), plotting average isotherms based on different measurements for the system water/ethanol/KCl. The authors concluded that the agreement is poor.

Despite the recent important demonstrations of the increasing interest in SLE data for electrolyte systems put into evidence by Lorimer (1993), Chiavone-Filho and Rasmussen (1993), Gomis et al. (1994), and Marcilla et al. (1995), among others, the SLE curiously did not receive, in the last decades, attention comparable to the VLE case. Those works enhanced the need of concentrating efforts in the experimental work in order to establish a reliable and consistent database, since the published data is very irregular concerning the systems and conditions studied, without any systematized work.

3.2.2 Experimental Methods

The methods presented in the literature to measure the solubility of electrolytes in liquids may generally be classified as analytical or synthetic methods. In order to establish an experimental set up, those methods were extensively reviewed and the main relevant topics are indicated in the following sections.

3.2.2.1 Analytical Methods

This method consists in the preparation of a saturated solution at constant temperature. Usually a glass cell is charged with known weighted amounts of all components with a small excess of salt over the previously estimated solubility value. To reach the solution equilibrium conditions stirring is promoted for a period of time, then the solution is allowed to settle, and after a sample is withdrawn for analysis using a convenient and reliable method.

The analytical method has been widely applied for the measurement of salt solubilities in mixed solvent systems but care should be taken with the cell design, temperature control, sampling procedure, determination of the optimum times for stirring and settling, and obviously with the analytical technique for composition analysis.

Different kind of glass cells have been suggested in the literature (Lombardo, 1967; Malahias and Popovych, 1982; Mydlarz et al., 1989). To control the solution temperature the cells are immersed in a thermostated water bath or, if they are jacketed glass cells, thermostated water from the bath is forced to circulate inside the jacket.

The cell volume varies approximately between 25-200 cm^3, which according to Lombardo (1967) depends both on the amount of the required sample or the expected solubility. The major drawback of those cells is that temperature is not measured directly in the solution but in the bath, which may cause some uncertainties in the registered temperature. Chiavone-Filho and Rasmussen (1993), who designed a cell allowing the direct measurement of the temperature in the solution, overcame this problem.

Stirring times to attain the equilibrium have been reported since a few hours up to several days, while for the settling time a period between ¼ h to 1 h is usually considered enough (Malahias and Popovych, 1982; Chianese et al., 1986; Mydlarz et al., 1989; Chiavone-Filho and Rasmussen, 1993). Therefore, to be able to perform quick and trustworthy measurements the stirring time should be previously obtained.

Several analytical techniques have been applied to determine the liquid phase composition. Frequently only the salt content is measured by gravimetry, but potentiometric titration or flame emission spectrophotometry (Labban and Marcus, 1991; Dash et al., 1991) or densimetry (Mydlarz and Jones, 1991), among others, have been used. It is commonly accepted though, that the gravimetric technique is suitable for that type of solubility measurements with reproducibility better than 0.1 mass % (Chianese et al., 1986; Chiavone-Filho and Rasmussen, 1993; Cartón et al., 1994; Marcilla et al., 1995), much better than the reproducibility obtained with other analytical methods.

3.2.2.2 Synthetic Methods

The basic principle of this kind of method is that the solution composition is known during the whole measurement. The cell is charged with weighted amounts of solvent and salt, with a little excess of salt over the estimated value, being the desired state when all the salt is completely dissolved. This is achieved either, by changing the temperature (polythermal synthetic method) or by adding a known amount of solvent (isothermal synthetic method). The main advantage of this method is that no analytical technique is necessary to measure the saturation composition.

The polythermal synthetic method has been very useful for salt solubility measurements in water/salt or water/salts systems (Potter and Clynne, 1978; Farelo et al., 1993), but a few examples may be encountered for the mixed solvent ones (Srivastava et al., 1985; Barata and Serrano, 1997). The method is extremely time-consuming since the temperature increments

are made progressively smaller as the number and size of existing crystals decrease; the heating rate is about 0.1K/h near the equilibrium point.

To monitor the solubility limit a property like conductivity can be used (Srivastava et al., 1985), but the visual method is mostly applied, that is, the equilibrium state is considered to be reached when, under a strong back-light, no salt particles can be seen (Potter and Clynne, 1978; Farelo et al., 1993). According to Potter and Clynne (1978), their designed apparatus has a sensitivity of 1mg of salt in the identification of the disappearance of the last crystal.

It is important to refer that to avoid the change of bulk composition by solvent evaporation due to the long measurement time, a layer of silicone oil is used to seal the cell.

The philosophy beyond the isothermal synthetic method is the same as for the preceding method, but a change on the composition of the solution is used instead. Mullin and Šlpek (1981) designed a solubility apparatus for mixed solvent systems. The solvent quantities are added to the mixture at hourly intervals (maximum 1 cm^3), drop by drop, towards the end point. The precision of this method is around 0.5%. Tavares et al. (1999) designed an experimental set up using this method. The equilibrium detection is not done by a visual technique, but using a faster one based on the thermal effects associated with the phase transformations that occur in the mixture. The method seems to give high deviations from accepted values for salt solubilities in water.

Recently, Zhang et al. (1998) combined the polythermal and isothermal synthetic methods to improve the measurements and also made them faster. The standard deviation of their experiments is around 0.35 mass %.

3.2.3 Conclusive Statements

The occurrence of a great lack of valid experimental salt solubility data leads to the implementation of an experimental programme. The data measurement is, as previously remarked, one of the important objectives of this work.

Besides water, two other solvents were chosen: methanol and ethanol. Ethanol is inexpensive and environmentally friendly and it is commonly used for many precipitation processes in biochemical industries, like the protein precipitation, improving yield and purity. Methanol is not suitable for biochemical industries but has been widely used for extractive crystallization

in the chemical industry. In fact, both solvents origin a sharp decrease of the solubilities and are suitable for that kind of processes.

Concerning the salts NaCl, KCl, KBr and NaBr were selected for two main reasons. They exhibit different trends for their solubilities in water and have been extensively studied regarding other thermodynamic properties like osmotic and mean ionic activity coefficients in water or VLE in mixed solvents. These two factors permit the validation of a general method for correlation and/or prediction of solubilities that might be extended to other systems.

A programme for systematic measurements, hardly ever found in the literature, is then implemented to measure the solubility of salts in the single solvents and in the binary mixed solvents water/methanol, water/ethanol and methanol/ethanol.

An analytical gravimetric method was chosen to perform the measurements. This has several advantages over the synthetic methods: the solubility can be determined at a desired temperature and solvent composition (those are the changing variables in the synthetic methods), it is faster if the stirring time required to attain the equilibrium is not high. Even more, the synthetic methods are not suitable if the solubility change with the temperature or solvent composition is not pronounced as is the case for systems with NaCl and probably for some mixed solvent composition ranges for all salts.

As already expressed the principal advantage of the synthetic methods is that no analytical technique is necessary to obtain the saturation composition. However, the gravimetric is an inexpensive and easy method that has been successfully and widely applied for mixed solvent systems with reliable results.

3.3 Experimental Procedure

In the following sections detailed information is given about the experimental procedure. Depending on the solvent, the maximum temperature studied in this work is 353.15 K (water), 333.15 K (methanol) and 348.15 K (ethanol). For water/methanol and methanol/ethanol mixed solvents the study was carried out at 298.15 and 323.15 K, while for water/ethanol mixed solvents, experiments were also performed at 348.15 K. The lower temperature is independent of the studied solvent and was chosen to be 298.15 K.

3.3.1 Materials

In all experiments distilled-deionized water was used. All the other chemicals were supplied by Merck; the four salts (NaCl, KCl, NaBr and KBr), with a purity higher than 99.5%, and the solvents, methanol and ethanol, with a minimum purity of 99.8%, were employed with no further purification.

It should be mentioned that to avoid the water salt contamination, salts were dried at 393.15 K in a drying stove for a period longer than 2 days, before use.

3.3.2 Apparatus Description

The designed jacketed cell for the equilibrium measurements is based on the one by Chiavone-Filho and Rasmussen (1993). It is appropriate for SLE in electrolyte and non-electrolyte systems, as well as for LLE measurements.

The volume of the cell and the dimensions and configuration were fixed considering the following factors:

- The inner volume should be such that it allows enough volume samples for the very low solubility measurements. In fact, if the solubility is low, like it is generally for salts in alcohols, the gravimetric method is not so appropriate since the remaining dried salt to be weighted is insignificant, giving rise to errors due to the sensitivity limits of the electronic balance. The cell volume is about 120 cm^3, enabling large volume samples without dragging solid salt from the bottom. The sampling process is described in section 3.3.3.

- In the top, the cell has two vertical orifices with diameter equal to 1 cm. One is for the mercury thermometer to directly measure the solution temperature and the other to take the samples. The lateral orifices for entry (at the bottom) and exit (at the top) of the heating water are placed in opposite sides, avoiding sluggishness.

- The inner diameter of the cell is established in order that the mixing process achieved by the magnetic bar (3 cm length) promotes efficient contact between the solid and liquid phases. The cell inner diameter and height were fixed at 5 and 6.5 cm, respectively. The height of the cell meets the condition that the thermometer should be sufficiently immersed in the solution.

- The external dimensions of the cell are 8 cm for the diameter and 11 cm for the height. In this way the renewal of circulating heating water is sufficiently fast to easily maintain the solution temperature within $\pm 0.1\,K$.

The solution temperature is known by direct reading with a mercury thermometer (Amarell Precision) with 0.1 °C resolution. The thermometer was calibrated every 4 months by CATIM laboratory (Porto), over the temperature range 293-363 K and the estimated accuracy is $\pm 0.1\,K$.

The jacketed glass cell, built at Instituto Superior Técnico (Lisboa), is shown in Figure 3.3.

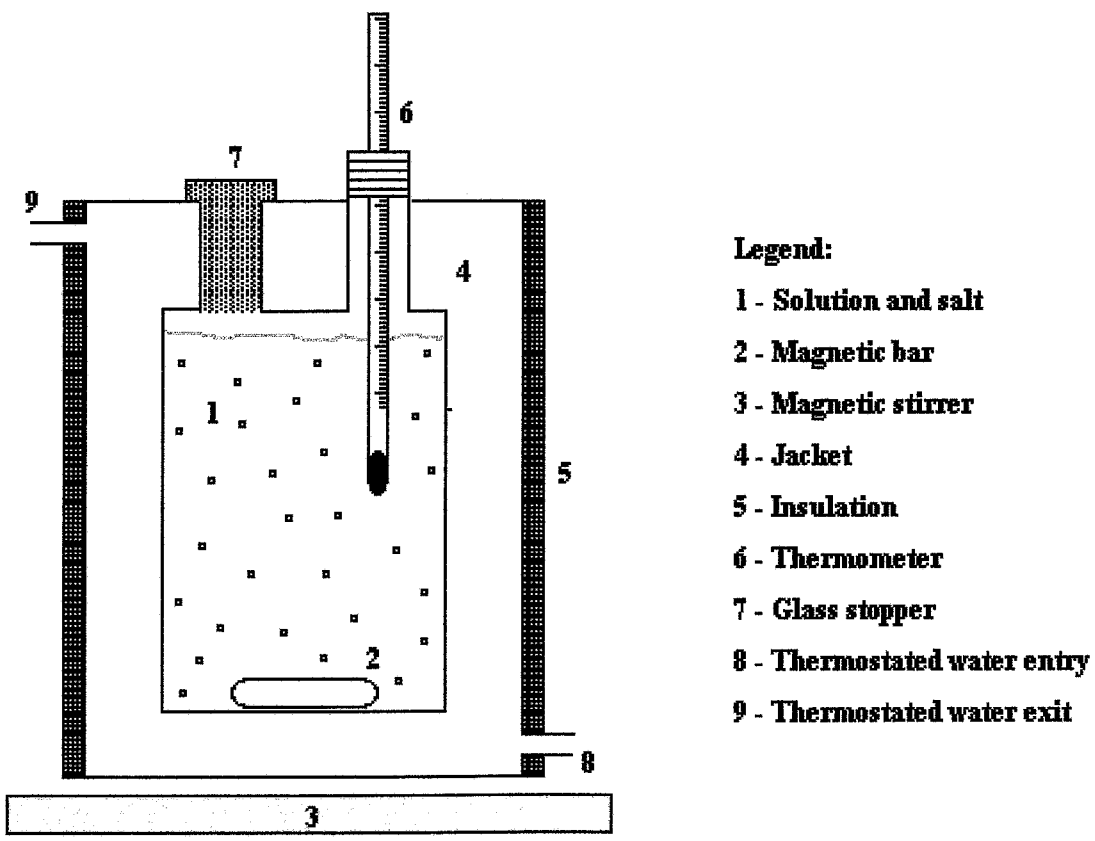

Figure 3.3 Cell for solubility measurements.

To feed the heating water to the cell jacket a thermostated water bath was used. The constant temperature bath is equipped with a digital controlled immersion circulator (Tempunit® TU-16D, Techne). The main features of that unit are temperature control stability and a maximum pumping flow of $\pm 0.005\,K$ and 10 dm^3/min, respectively, enabling the already indicated solution temperature control.

To efficiently promote the solubleness process, the phase mixing is achieved using a magnetic stirrer (Agimatic-N, Selecta) and a magnetic bar. The stirrer speed may be set between 60 and 1600 rotations per minute (rpm), but a speed around 600 rpm was chosen. The contact between the solid and liquid phases is then properly established, without breaking the crystals, preventing in this way, the formation of micro crystals and the subsequent supersaturation.

3.3.3 Sampling Procedure

Salt solubility usually rises with increasing temperature. Thus, if care it is not taken during the sampling, salt precipitation may easily occur. To avoid this undesired effect due to temperature changes, in this work a stainless steel heated jacket was designed and constructed at the Department of Chemical Engineering in Lyngby (Denmark), where the syringe is fitted, in order to preheat it at the desired temperature.

The jacket is connected to a variable transformer (V8HM, Zenith) previously calibrated in order to get a temperature in the syringe 5 K above the working temperature. Glass syringes of 5 cm^3 (Gastight #1005, Hamilton) were used and care was also taken to properly heat the needles.

For each determination usually 3 to 4 samples, of approximately 5 cm^3, are withdrawn from the saturated solution, then are inserted into a glass vessel (25 cm^3) with a ground-in glass stopper and immediately weighted. Details of the whole procedure are given in 3.3.5.

Adjustment of this sampling procedure was essential whenever the salt solubility attained extreme values: for salt solubilities lower than 0.5% (mass percentage) or higher than 45%. In those situations, instead of syringes, heated pipettes were used. The reasons for this modification lie in the fact that for low solubility measurements the gravimetric method is not so accurate since the amount of remaining dried salt in the glass vessel is too little, and only with bigger samples (25 cm^3) the desired accuracy can be achieved. On the other hand, it turned out that for high solubility measurements suction of saturated solution with the syringe

was frequently impracticable due to obstruction of the needle. In this last case a 10 cm^3 sample was picked from the solution with a pipette.

Simple sampling was carried out in the unusual cases where solubility decreases with temperature rising since no pre-heating was necessary.

3.3.4 Optimum Stirring Time Determination

In section 3.2.2.1 the stirring times indispensable for equilibrium, implemented by different authors were stated. However, high deviations in those values were detected even for the same kind of systems at the same conditions.

To establish the optimum time required to reach the equilibrium state, preliminary essays were made. That optimum time can be obtained by measuring the mass of salt dissolved after several time periods. Water was chosen for that purpose since it presents the higher solubility values for all the solutes, being therefore the expected solvent to present longer times to attain the equilibrium state. The measurements carried out at three different temperatures followed the usual procedure totally explained in the next section. The obtained results for NaCl and NaBr salts in water are summarized in Figure 3.4.

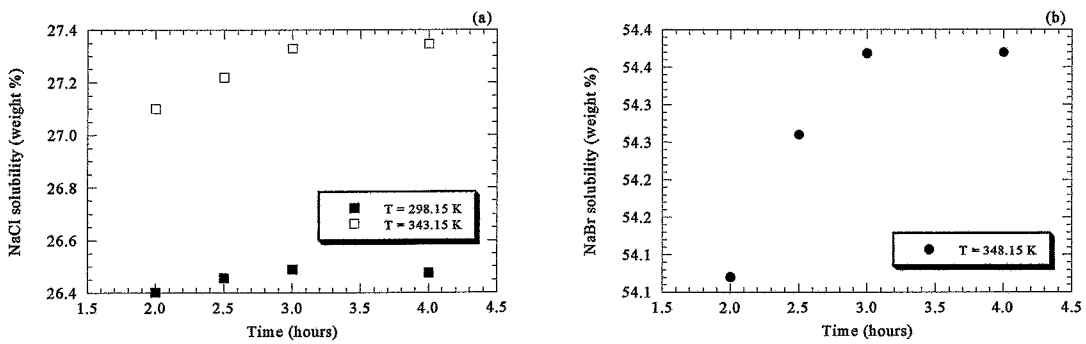

Figure 3.4 Solubility of salts in water versus stirring time: (a) NaCl (b) NaBr.

These previous essays enabled to conclude that 3 hours of stirring are enough to perform the equilibrium measurements.

3.3.5 Procedure

The following described procedure reports to a salt solubility measurement in a mixed solvent. Indeed, the one solvent measurement only differs in the solvent previous preparation and in the cooling cycle.

Desired amounts of each solvent, starting with the less volatile one, are weighted into a balloon-flask, in a 0.1 mg precision electronic balance (model A 200 S, Sartorius) to prepare approximately 110 g of solvent mixture. The resulting solution is vigorously shaked for 5 minutes to promote complete mixing. After, the dried salt (that was in the dehydrator) is quickly weighted into the cell in a small excess over the expected solubility limit. Immediately, the cell is charged with at least 75 g of the already prepared solvent, the magnetic bar is introduced, and the thermometer is placed in one of the top orifices. Then, the cell is conveniently closed and the stoppers wrapped with laboratory film to avoid solvent evaporation and the consequent change of the solvent composition.

The amount of the charged solvent mixture depends both on the solvent density and on the mass of the salt already in the cell. The wanted effect is to leave only a small free volume inhibiting the solution contamination by gas and solvent evaporation. The mass of salt added to the cell should be adequate since its excess may cause the determination of unreal overestimated solubilities and its deficit implies the cell opening to introduce more salt. Frequently, reliable salt solubility values are not available for mixed solvents, and those were estimated from the correspondent solubilities values in the pure solvent or from previous experimental results.

Afterwards, the solution in the cell is heated and its temperature controlled by circulating thermostated water, supplied by the constant temperature bath, in the jacket of the cell. The solution temperature is accurate within $\pm 0.1\,\mathrm{K}$. Simultaneously, stirring is started using the magnetic stirrer. In order to avoid the formation of micro crystals, normally the temperature is first set slightly above of the equilibrium temperature. Stirring lasts for 3 hours at the working temperature.

A cooling cycle was used for the temperatures 323.15 and 298.15 K, that is, the temperature was first set at 325.15 K and then the solubilities were measured at 323.15 and 298.15 K. It should be noticed that when doing a cooling cycle after the first sampling (at 323.15 K) fresh solvent mixture already prepared was added to the cell in order to decrease the amount of salt in the solid phase as well as the volume vapour phase over the liquid. The solubilities at 348.15 K were measured separately to avoid large solvent composition changes during the cooling cycle.

At the beginning of this section it was indicated that for single solvent measurements this cooling cycle is slightly different. Indeed, the procedure is similar to the one expressed above, but proper changes on the initial and final temperature values were done because solubilities were measured at several different temperatures as can be observed in section 3.4.1.

Additionally, as regards systems where the solubility decreases with rising temperature, like for instance the methanol/NaBr system, a heating cycle was used instead, but following a parallel sequence.

The magnetic stirrer is then turned off and the equilibrium saturated solution is allowed to settle for at least ½ h before sampling. The samples of the saturated solution are then inserted into glass vessels (25 cm^3) with a ground-in glass stopper and immediately weighted. As the gravimetric method is based in the difference between weights, the empty glass vessels had already been weighted.

The glass vessels are then stored and left to cool for about 1h and weighted again. During the experiments it was observed that, when the difference between the sample and the room temperatures is high, the value read in the balance was slowly increasing. In fact, the difference between those two measurements was sometimes higher than 4 mg, and only the last reading was considered for the calculations.

After, the total solvent evaporation is achieved in two stages. Initially, the samples are placed in a heating plate, at a temperature inferior to the boiling temperature of the most volatile component, to blandly evaporate most of the solvent. In this way, the dragging of small particles of salt by the solvent is prevented. The process enhances the formation of salt crystals in the glass vessel, that are then completely dried in a drying stove (Memmert) at 393.15 K.

The glass vessels are in the drying stove for periods longer than 3 days, and are cooled after in a dehydrator with silica gel for one day. Finally, they are weighted and the process is regularly repeated until a constant value is achieved. This trial and error process can, in some cases, take more than 3 weeks.

Each experimental point is an average of at least three different measurements obeying one of the following criteria:

If the solubility is higher than 10% (mass percentage) the reproducibility, measured by the quotient $2s/\text{solubility}*100$, should be better than 0.1 (*wt%*). The standard deviation (s), within a set of different experimental results is defined as,

$$s = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2} \tag{3.1}$$

where x_i is the experimental solubility of sample i and $\bar{x}$ is the arithmetical mean of n experimental results.

If the experimental solubility is less than 10% this criterion is difficult to attain and in this case an equivalent criterion is that the standard deviation should be lower than 0.005.

3.3.6 Method Reliability

In the last section the criteria to accept or not a set of experimental solubilities was given and it was observed that the reproducibility or precision is very good, but no indications about accuracy are given.

To check the method accuracy, three water/NaBr solutions with known salt concentration, lower than the solubility limit, were prepared and placed in the solubility cell. The procedure described above was carried out at 323.15 K, for each solution, enabling the measurement of the salt concentration by the gravimetric method. The obtained results and the deviations relatively to the true value are presented in Table 3.1.

Table 3.1 Comparison between true and measured salt concentration (weight %).

True Concentration	Measured Concentration	Deviation (%)
0.643	0.645	0.31
9.933	9.962	0.29
40.032	40.082	0.12

The measured values seem to be slightly higher (maximum deviation 0.31%) than the true salt concentration of the former solution. This might suggest systematic experimental operation errors due maybe to solvent evaporation, incomplete salt drying, or casual errors. However, the differences are quite acceptable and the method is therefore very reliable.

3.4 Experimental Measured Data

The measured solubility data are reported in the sections 3.4.1 to 3.4.3.

3.4.1 Binary Systems

In the Tables 3.2 to 3.4 the measured solubilities expressed in mass percentage (grams of salt per 100 grams of saturated solution –*wt%*–) of the salts in water, methanol and ethanol, are reported, respectively. The water/salt systems were studied in a temperature range between 298.15 and 353.15 K, while for systems with methanol the maximum temperature is 333.15K. The ethanol/salt systems were only studied at three different temperatures; 298.15, 323.15 and 348.15 K since the salt solubilities are too low or the temperature dependency is not pronounced.

From Table 3.2 it is possible to conclude that, at a given temperature, the solubilities of salts in water follow the sequence: NaBr > KBr > KCl > NaCl, except at 298.15 K where this sequence for the two less soluble salts is slightly inverted.

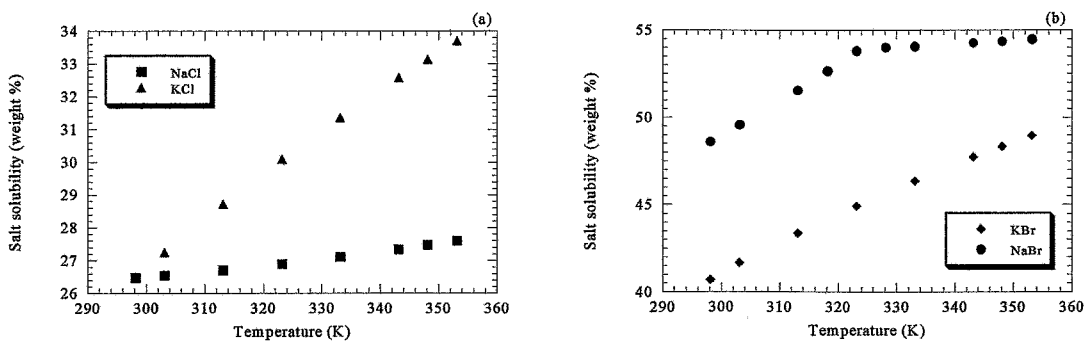

Figure 3.5 *Solubility of salts in water at different temperatures: (a) NaCl and KCl (b) KBr and NaBr.*

Table 3.2 Solubility (wt%) of salts in water at different temperatures.

Temperature (K)	NaCl	NaBr	KCl	KBr
298.15	26.483	48.620	26.476	40.713
303.15	26.550	49.583	27.257	41.670
313.15	26.701	51.571	28.728	43.359
318.15		52.673		
323.15	26.889	53.838	30.094	44.932
328.15		54.015		
333.15	27.106	54.087	31.366	46.360
343.15	27.338	54.281	32.582	47.725
348.15	27.478	54.369	33.146	48.349
353.15	27.602	54.495	33.709	48.961

Figure 3.5 illustrates the change of the salt solubility in water due to temperature changing. It may be observed that for all systems the salt solubility increases with rising temperature, but the trend is very different from system to system. In fact, for the salts KCl and KBr this behaviour is well pronounced, while for the NaCl solubility it is not.

The trend is more odd for the water/NaBr system; up to 323.15 K the solubility increasing is very evident while beyond that value it is almost constant. The observed breaking behaviour corresponds to a solid phase transition. According to Rard and Archer (1995), the transition occurs at 323.98 K, and below that temperature the solid phase is $NaBr.2H_2O$ while above it the solid phase is NaBr.

The experimental results measured in this work can be used to estimate the transition temperature by making two linear fits, one with the experimental results until 323.15 K and the other with the results for temperatures above this one. The intersection of those two lines should give the desired temperature. The obtained value using the data presented in Table 3.2 is 324.00 K, which may be a good indication of the data quality.

From Table 3.3 it is possible to observe that the previous ordering regarding the solubility of salts in water at a given temperature is completely reversed between NaCl and KCl for the methanol/salt systems.

The temperature effect on the solubility is again very different from salt to salt. As can be seen in Figure 3.6 the salts NaCl and NaBr exhibit an inverse salt solubility temperature dependency; the salt solubility decreases with rising temperature. This effect is more pronounced for the salt NaBr. The other two salts (KCl and KBr) are, lets say, well-behaved.

Table 3.3 Solubility (wt%) of salts in methanol at different temperatures.

Temperature (K)	NaCl	NaBr	KCl	KBr
298.15	1.375	14.938	0.539	2.063
303.15	1.360	14.754	0.554	2.150
313.15	1.310	14.461	0.593	2.324
323.15	1.235	14.196	0.630	2.503
333.15	1.220	13.941	0.670	2.672

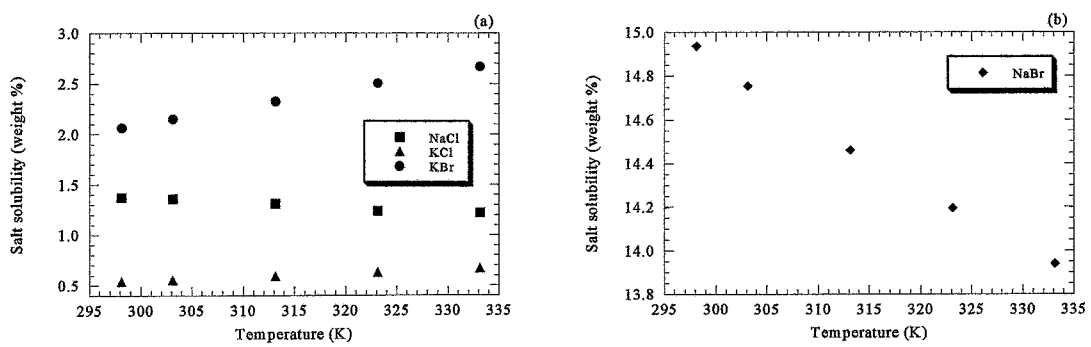

Figure 3.6 Solubility of salts in methanol at different temperatures: (a) NaCl, KCl and KBr (b) NaBr.

This unusual effect of the temperature on the solubility, although unforeseen for a given system, may be explained both by Debye-Hückel and ion association Bjerrum theories (Robinson and Stokes, 1970), since at such low ionic concentrations the electrostatic interactions are more pronounced and association is favoured by the lower dielectric constant.

As can be seen in Table 3.4 the salt solubilities in ethanol obey the ordering expressed for methanol, that is, NaBr > KBr > NaCl > KCl. Now only NaBr shows the inverse temperature behaviour.

Table 3.4 Solubility (wt%) of salts in ethanol at different temperatures.

Temperature (K)	NaCl	NaBr	KCl	KBr
298.15	0.055	2.496	0.034	0.135
323.15	0.065	2.416	0.039	0.185
348.15	0.077	2.297	0.049	0.232

Finally it should be noticed that for all studied salts the expected solubility sequence regarding the solvents, water > methanol > ethanol, obeys the predicted order based on the dielectric solvent constant.

3.4.2 Ternary Systems

The measured solubility data for mixed two-solvent systems are presented in the following sections, divided according to the mixed solvent studied. The solubility is, like for the binary systems, expressed in terms of mass percentage (*wt%*), while the solvent composition is expressed in water (w'_{water}) or methanol ($w'_{methanol}$) mass percentage in salt free basis.

3.4.2.1 Water/Methanol Systems

The experimentally measured solubilities of NaCl, KCl, NaBr and KBr in water/methanol mixed solvent systems at 298.15 and 323.15 K, are given in Table 3.5.

The observed order for the solubilities in water/methanol solvent mixtures follows, in general, the sequence: NaBr > KBr > NaCl > KCl. An exception to this appears for NaCl and KCl at 323.15 K for water concentrations in the mixed solvent higher than 60%.

Table 3.5 Solubility of salts in water/methanol solvent mixtures.

Water + Methanol + NaCl			Water + Methanol + KCl		
	Salt Solubility (*wt%*)			Salt Solubility (*wt%*)	
w'_{water}	298.15 K	323.15 K	w'_{water}	298.15 K	323.15 K
10.00	1.998	2.098	10.00	0.825	1.123
20.01	3.228	3.552	20.00	1.493	2.150
40.00	7.244	7.929	40.00	4.463	6.285
50.00	9.969	10.751	50.00	6.874	9.433
60.00	12.939	13.767	60.00	9.482	13.094
80.00	19.499	20.212	80.00	17.503	21.472
90.00	22.945	23.521	90.00	21.924	25.868
Water + Methanol + NaBr			Water + Methanol + KBr		
	Salt Solubility (*wt%*)			Salt Solubility (*wt%*)	
w'_{water}	298.15 K	323.15 K	w'_{water}	298.15 K	323.15 K
10.00	18.772	18.532	10.00	3.124	4.258
20.00	23.524	23.465	20.00	5.206	7.303
30.00	28.258	28.326	30.00	8.350	11.484
40.00	32.634	32.829	40.00	12.291	16.326
49.98	35.862	36.931	50.00	16.662	21.424
59.98	38.339	40.793	60.00	21.334	26.506
69.99	41.070	44.306	70.00	26.131	31.435
79.99	43.716	47.686	80.00	31.033	36.210
89.99	46.245	50.910	90.00	35.833	40.660

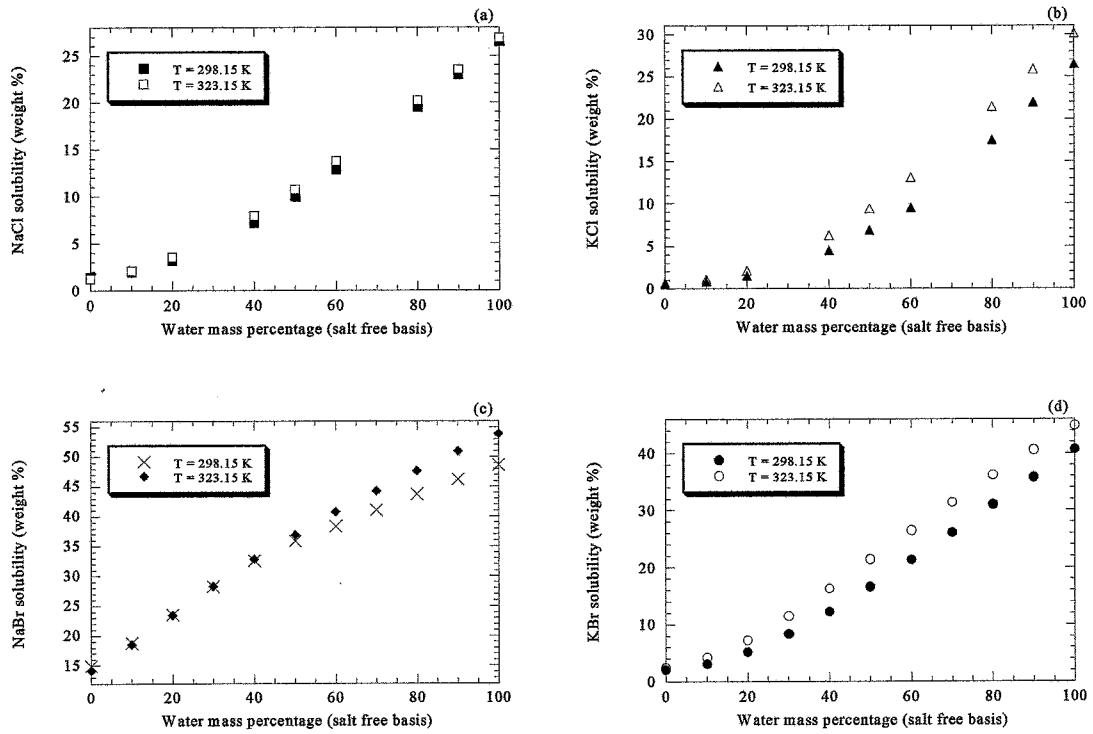

Figure 3.7 *Solubility isotherms in water/methanol solvent mixtures: (a) NaCl (b) KCl (c) NaBr (d) KBr.*

From Figure 3.7 it is possible to observe, for all systems, a sharp decrease of the electrolyte solubility as long as the methanol concentration rises in the mixed solvent. However, the curve shape is quite different for water/methanol/NaBr system: while for the other systems the curves are concave, for that particular case the curves are convex.

Even more interesting is the change of the solubility with temperature for that particular system. Usually, the solubility rises with increasing temperature, being the effect more pronounced as the water concentration in the mixed solvent rises and for systems involving the potassium salts.

The system water/methanol/NaBr at very low water concentration has, like expected, a lower solubility at a higher temperature, since the NaBr solubility in methanol is a decreasing function of the temperature. However, the water/NaBr system has, in the temperature range studied, a large solubility increase, but a notorious difference for mixed solvent systems is only observed for water concentration higher than 50%. It can be noticed that in a different magnitude scale the same happens for NaCl single solvent systems, but for the mixed solvent, despite the difference is not large, the differentiation is more perceptible in almost all the composition range.

3.4.2.2 Water/Ethanol Systems

The experimentally measured solubilities of NaCl, KCl, NaBr and KBr in water/ethanol mixed solvent systems at 298.15, 323.15 and 348.15 K, are given in Tables 3.6 and 3.7.

The observed rank for the solubilities in water/ethanol solvent mixtures follows the sequence: NaBr > KBr > NaCl > KCl. An inversion to this occurs for NaCl and KCl at 323.15 and 348.15 K for water concentrations in the mixed solvent slightly higher than 60% and 40%, respectively.

From Figure 3.8 it is possible to observe the same behaviour as for the preceding solvent mixture, that is, a sharp decrease on the solubility as long as the ethanol concentration rises in the mixed solvent.

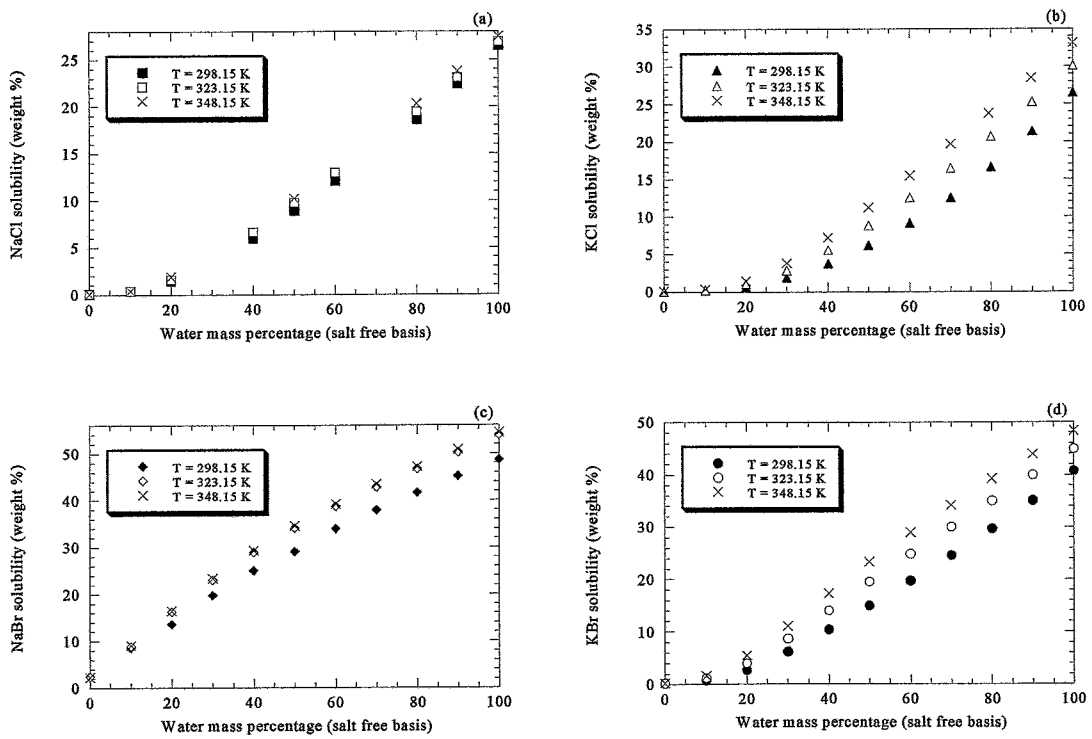

Figure 3.8 Solubility isotherms in water/ethanol solvent mixtures: (a) NaCl (b) KCl (c) NaBr (d) KBr.

Table 3.6 Solubility of NaCl and KCl in water/ethanol solvent mixtures.

Water + Ethanol + NaCl				
	Salt Solubility (*wt%*)			Salt Solubility (*wt%*)
w'_{water}	298.15 K	323.15 K	w'_{water}	348.15 K
10.00	0.350	0.368	10.00	0.404
20.00	1.408	1.596	20.00	1.903
40.00	6.008	6.650	50.00	10.216
50.00	8.910	9.777	80.00	20.292
60.00	12.066	12.953	89.96	23.758
80.00	18.602	19.442		
90.00	22.397	23.037		
Water + Ethanol + KCl				
	Salt Solubility (*wt%*)			Salt Solubility (*wt%*)
w'_{water}	298.15 K	323.15 K	w'_{water}	348.15 K
10.00	0.164	0.254	10.00	0.344
20.00	0.685	1.064	20.00	1.458
30.00	1.874	2.834	29.99	3.796
40.04	3.759	5.544	40.00	7.206
50.00	6.198	8.828	50.00	11.189
60.00	9.123	12.519	60.00	15.415
70.00	12.544	16.436	70.00	19.666
80.00	16.589	20.666	79.44	23.745
89.98	21.352	25.225	89.81	28.452

Table 3.7 Solubility of NaBr and KBr in water/ethanol solvent mixtures.

Water + Ethanol + NaBr				
	Salt Solubility (*wt%*)			Salt Solubility (*wt%*)
w'_{water}	298.15 K	323.15 K	w'_{water}	348.15 K
10.00	8.527	8.840	10.00	9.051
20.00	13.648	16.277	20.00	16.491
30.00	19.808	23.009	30.00	23.299
40.00	25.124	28.905	40.00	29.328
50.00	29.119	34.121	50.00	34.637
60.00	34.007	38.689	60.00	39.224
70.00	37.928	42.876	70.00	43.501
80.00	41.662	46.706	79.99	47.266
90.00	45.162	50.276	89.99	50.892
Water + Ethanol + KBr				
	Salt Solubility (*wt%*)			Salt Solubility (*wt%*)
w'_{water}	298.15 K	323.15 K	w'_{water}	348.15 K
10.00	0.734	1.141	10.00	1.593
20.00	2.678	4.010	20.02	5.430
30.00	6.112	8.671	30.00	11.060
40.00	10.374	14.043	39.97	17.262
50.00	14.977	19.542	49.95	23.317
59.99	19.730	24.908	60.00	29.023
70.00	24.574	30.016	69.92	34.214
80.00	29.656	35.015	80.06	39.238
90.00	35.121	39.991	90.00	43.929

The effect of the temperature on the solubility is again more pronounced for the potassium salts, but also for the water/ethanol/NaBr between 298.15 and 323.15 K. In fact, the temperature effect on the NaBr solubility in water/methanol mixed solvent, for the same temperature range, only becomes evident for a water composition in the solvent higher than 50% while for water/ethanol mixed solvent the differentiation happens for all compositions.

Like for water/ethanol/NaCl system in the temperature range between 323.15 and 348.15 K the effect of the temperature on the solubility of NaBr in the water/ethanol solvent mixture is much less obvious, in all composition range.

3.4.2.3 Methanol/Ethanol Systems

The experimentally measured solubilities of NaCl, KCl, NaBr and KBr in methanol/ethanol mixed solvent systems at 298.15 and 323.15 K, are given in Table 3.8. The observed rank for the solubilities in methanol/ethanol solvent mixtures follows the sequence: NaBr > KBr > NaCl > KCl.

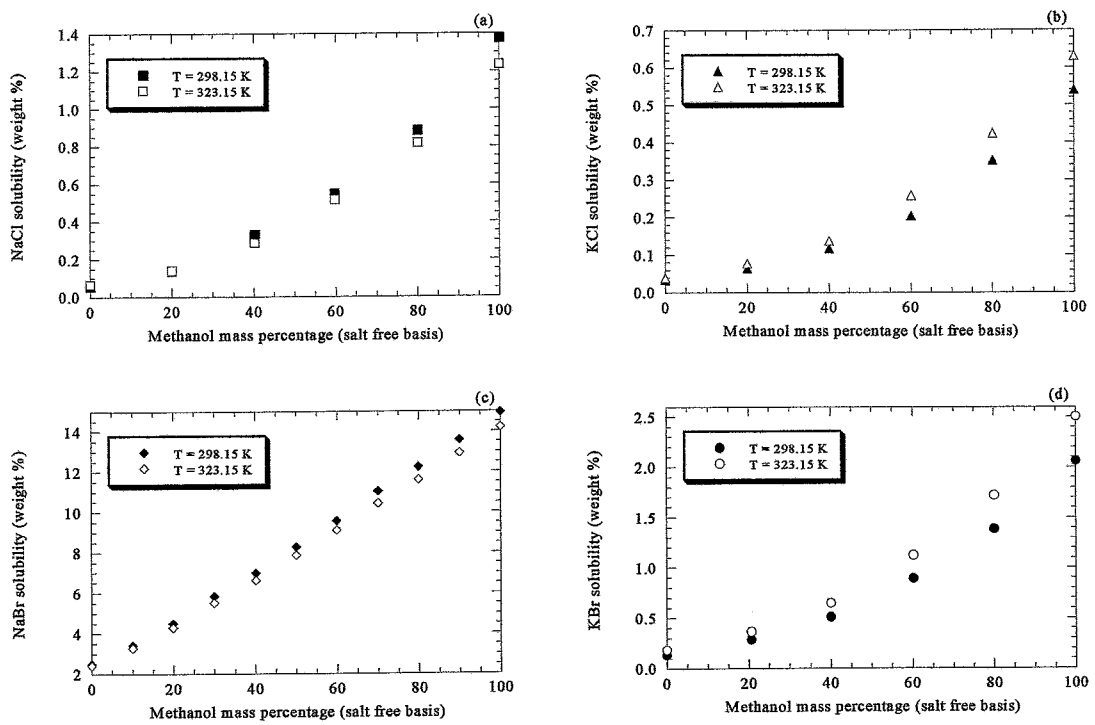

Figure 3.9 Solubility isotherms in methanol/ethanol solvent mixtures: (a) NaCl (b) KCl (c) NaBr (d) KBr.

The solubility of salts in the methanol/ethanol solvent mixtures is much lower than in the preceding systems and decreases with the increase of the ethanol concentration in the mixture. Unless for the NaBr salt, the solubilities are very small.

Table 3.8 Solubility of salts in methanol/ethanol solvent mixtures.

Methanol + Ethanol + NaCl			Methanol + Ethanol + KCl		
	Salt Solubility (*wt%*)			Salt Solubility (*wt%*)	
$w'_{methanol}$	298.15 K	323.15 K	$w'_{methanol}$	298.15 K	323.15 K
20.01	0.139	0.140	20.01	0.065	0.078
40.18	0.331	0.288	39.95	0.117	0.138
59.77	0.548	0.517	60.11	0.204	0.259
80.01	0.885	0.818	80.15	0.352	0.424
Methanol + Ethanol + NaBr			Methanol + Ethanol + KBr		
	Salt Solubility (*wt%*)			Salt Solubility (*wt%*)	
$w'_{methanol}$	298.15 K	323.15 K	$w'_{methanol}$	298.15 K	323.15 K
10.07	3.406	3.264			
19.87	4.497	4.287	20.60	0.286	0.369
30.01	5.835	5.522			
40.13	6.985	6.636	39.99	0.513	0.652
50.03	8.266	7.873			
59.96	9.579	9.110	60.25	0.892	1.124
70.00	11.033	10.438			
79.97	12.226	11.603	80.01	1.386	1.721
89.99	13.568	12.918			

In Figure 3.9 it is shown the inverse temperature behaviour of the sodium salts. Once more, the solubility of NaBr has a different behaviour from the other salts since the shape of the curves is almost linear while for the others is clearly concave.

3.4.3 Quaternary Systems

Usually industrial processes deal with multisalt-multisolvent mixtures. Therefore, to further check the predictive capabilities of the models developed in this work, which will be presented in chapter 4, some measurements were also carried out for quaternary systems at 313.15 K.

The systems studied were water/methanol/ethanol/KCl or KBr at fixed ethanol/methanol ratios. Table 3.9 shows the measured data, which are plotted in Figure 3.10.

Table 3.9 Solubility of KCl and KBr in water/methanol/ethanol solvent mixtures at 313.15K.

Water + Methanol + Ethanol + KCl			Water + Methanol + Ethanol + KBr		
w'_{water}	$\frac{w'_{ethanol}}{w'_{methanol}}$	Salt Solubility (*wt%*)	w'_{water}	$\frac{w'_{ethanol}}{w'_{methanol}}$	Salt Solubility (*wt%*)
00.00	4.002	0.073	00.00	1.000	0.790
19.45	3.996	0.955	20.00	1.001	4.553
40.00	4.000	4.833	40.00	1.001	13.277
60.00	4.001	11.226	59.93	1.000	23.492
80.00	3.999	19.282	79.98	1.001	33.631

$w'_{ethanol}$ is the ethanol mass percentage in the mixed solvent (salt free basis).

3.4.4 Critical Analysis

The quality of the measured data may be investigated comparing it with literature values reported in the compilation books published by Stephen and Stephen (1963; 1964), Linke and Seidell (1958; 1965) and in the open literature: for the water/salt binary systems the comparisons can be easily done due to the extensive amount of published data. However, for the other systems, data at temperatures different from 298.15 K is not available which makes difficult or even impossible the confrontation of the obtained experimental results.

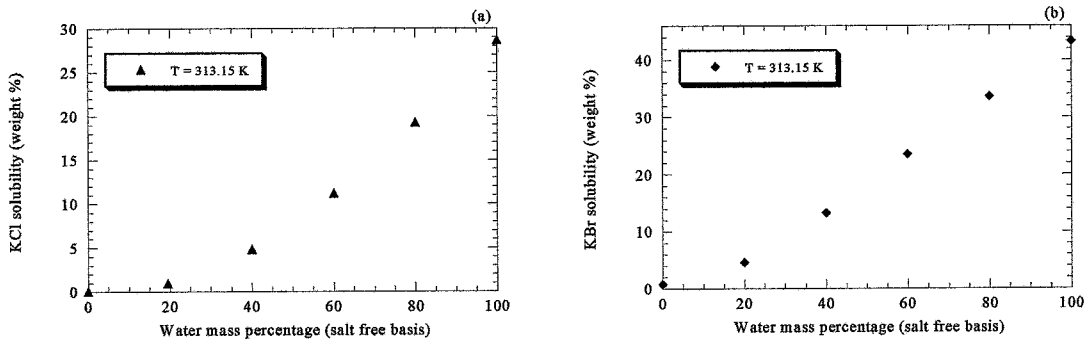

Figure 3.10 Solubility isotherms in water(1)/methanol(2)/ethanol(3) solvent mixtures: (a) KCl with $w_3'/w_2' = 4.00$ *(b) KBr with* $w_3'/w_2' = 1.00$.

In some cases the amount of consistent data presented in the compilation books is enough to make an average curve fit for a better graphical comparison with the more recent published data. That is shown, for instance, in Figures 3.11 and 3.12 for the systems water/NaCl and water/KCl, respectively. In fact, for these two particular systems it was possible to find more recent published data which are confronted with the solubilities measured in this work and the average of those found in the above-mentioned compilation books.

From Figure 3.11 it is possible to observe the good agreement of the data even if the solubilities measured in this work are systematically higher (around 0.05g of NaCl per 100g of solution) when compared with the values of Farelo et al. (1993). Although the values reported by Farelo and collaborators are clearly in better concordance with the average curve, they have used the polythermal synthetic method, which is not the most adequate since the temperature exhibits little influence on the NaCl solubility (Chianese et al., 1986). It seems this is the main reason for the unexpected irregular trend shown using their experimental data, which does not happen for the water/KCl system solubilities reported by the same authors, as presented in Figure 3.12.

Comparing the solubilities measured here and the ones reported by Farelo et al. (1993), for the system water/KCl at different temperatures, in Figure 3.12 it is possible to see a better agreement than for the previous system. Now, the systematic higher deviations do not occur, but instead a slight deviation change in the studied temperature range. The solubilities measured by Zhang et al. (1998) with a new method combining both the synthetic methods explained in 3.2.2.2 are also displayed, showing greater deviations and a trend a little bit odd. For the other water/salt systems it was also possible to find good agreement, as can be observed from Figures 3.13 and 3.14.

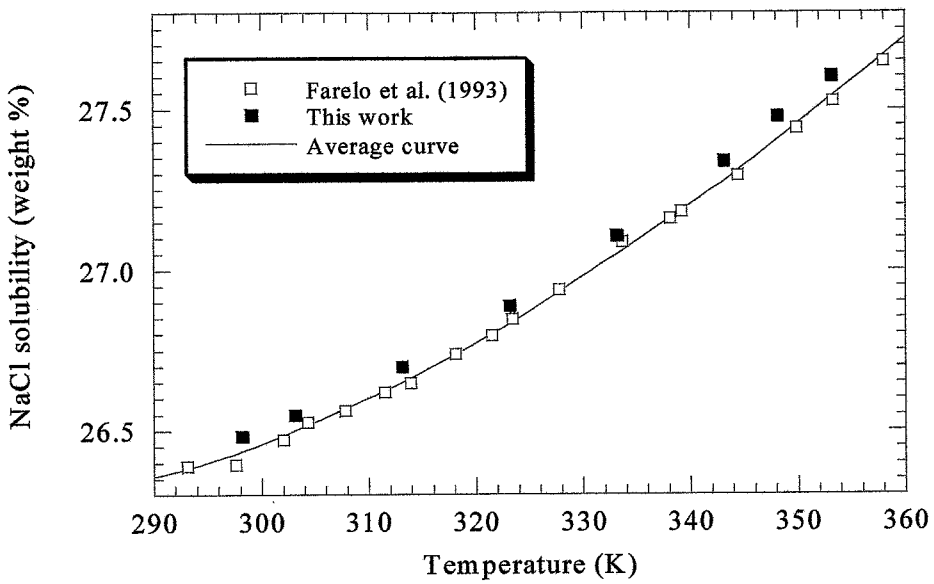

Figure 3.11 Comparison of the solubility of NaCl in water at different temperatures.

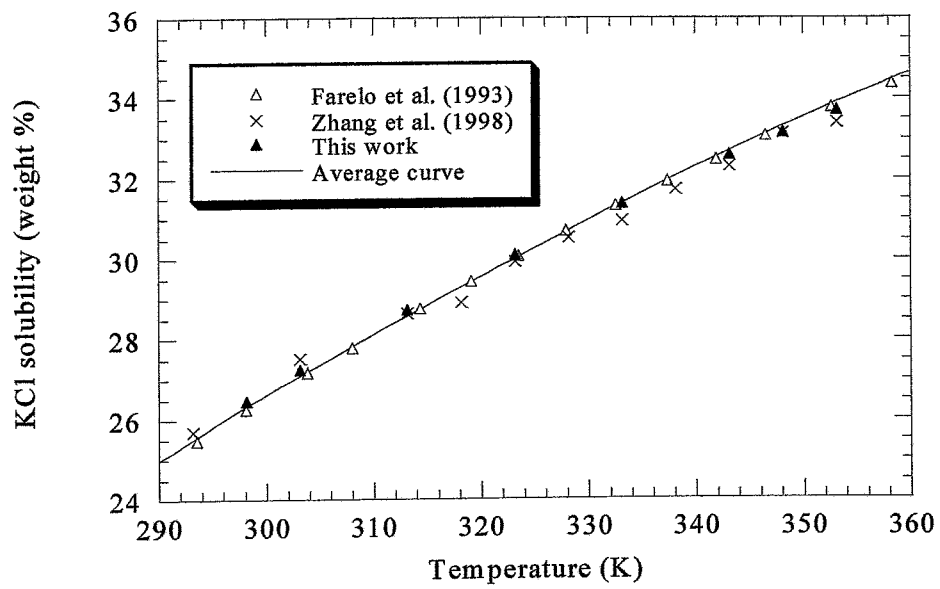

Figure 3.12 Comparison of the solubility of KCl in water at different temperatures.

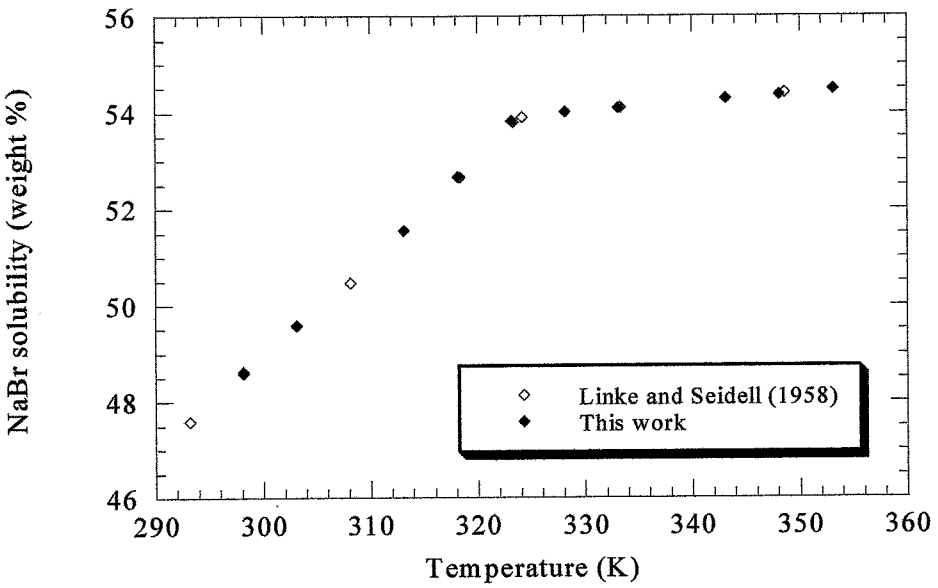

Figure 3.13 Comparison of the solubility of NaBr in water at different temperatures.

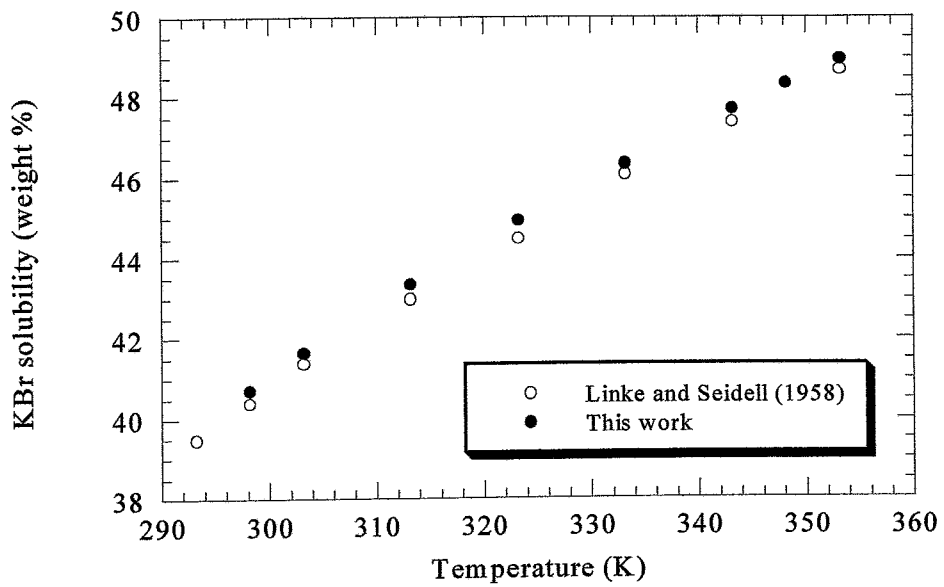

Figure 3.14 Comparison of the solubility of KBr in water at different temperatures.

It has already been mentioned that the solubilities of salts in alcohols at different temperatures are almost unknown. Thus, the same kind of comparison is quite difficult to make for the alcohol/salt systems. As can be seen in Figure 3.15 the measured solubilities of KBr in methanol are in accordance with the ones published by Lloyd et al. (1928), but for the methanol/NaBr system the same authors presented values much different from those obtained in this work.

Unfortunately, no reliable or more recent data were found for both systems to be able to carry out a better data evaluation. In this way, a comparison for the solubilities values at 298.15 K is presented in Table 3.10. For each salt, an interval for the values found in the compilation book by Stephen and Stephen (1963; 1964), which may differ more than 8%, the values obtained in this work, and some from the open literature are given.

All the solubilities measured in this work are very acceptable, but some uncertainty arises for the NaBr solubility in methanol; the value reported by Stenger (1996), obtained at 296.15 K, is very different from the one measured in this work at 298.15 K. Despite the working temperatures are different, such a discrepancy in a so narrow temperature range is suspicious. However, the data published for the water/methanol/NaBr system at 298.15 K, shown in Figure 3.16, support the measured values. Figure 3.16 also compares the solubility of KCl in water/methanol solvent mixtures and a higher consistency between the values is achieved. It should be mentioned that the measured solubilities by Malahias and Popovych (1982) were also carried using a gravimetric method but the time to achieve the equilibrium was taken as one week.

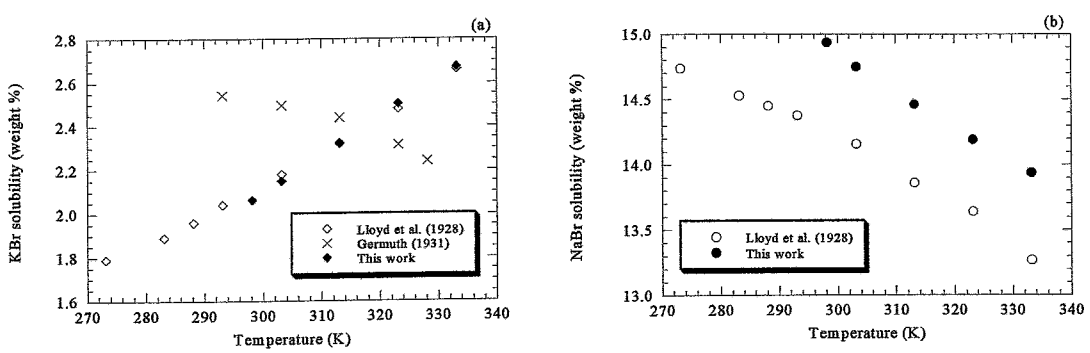

Figure 3.15 Comparison of the solubility of salts in methanol at different temperatures: (a) KBr (b) NaBr.

Table 3.10 Solubilities (weight %) of salts in methanol at 298.15 K.

	Chloride	Bromide
Sodium	1.29-1.381[a] 1.375[b] 1.370[c]	14.79-15.588[a] 14.938[b] 14.384[d]
Potassium	0.52-0.563[a] 0.539[b] 0.524[e]	2.07-2.12[a] 2.063[b]

[a]Stephen and Stephen (1963; 1964); [b]This work; [c]Wagner et al. (1998)
[d]Stenger (1996) –at 296.15 K–; [e]Malahias and Popovych (1982)

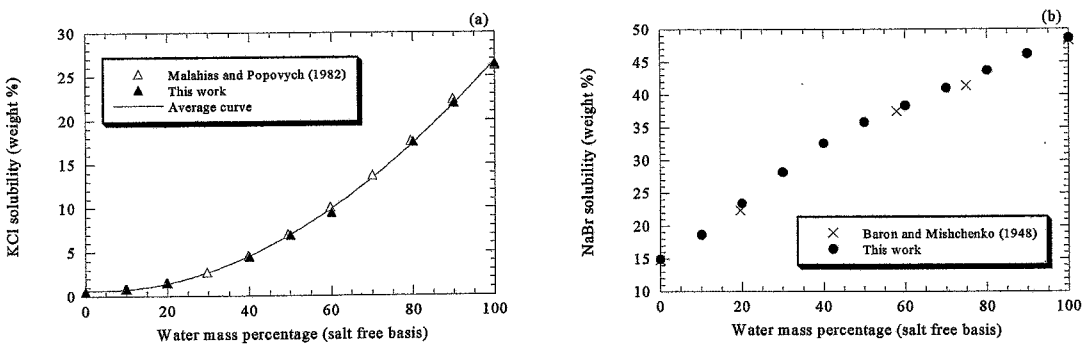

Figure 3.16 Comparison of the solubility of salts in water/methanol mixtures at 298.15K: (a) KCl (b) NaBr.

The solubility of salts in ethanol is also very difficult to compare and a similar procedure like that presented for methanol/salt systems at 298.15 K is given in Table 3.11. Again, the solubilities measured in this work are consistent with other published data.

Unless concerns the NaBr salt, for the others water/ethanol/salt systems it was possible to compare the experimental solubilities with more recent data.

Table 3.11 Solubilities (weight %) of salts in ethanol at 298.15 K.

	Chloride	Bromide
Sodium	0.065-0.066[a] 0.055[b] 0.068[c]	2.261-2.349[a] 2.496[b]
Potassium	0.022-0.0294[a] 0.034[b] 0.024[d] 0.045[e]	0.135-0.142[a] 0.135[b] 0.22[e]

[a]Stephen and Stephen (1963; 1964); [b]This work; [c]Marcilla et al. (1995)
[d]Chiavone-Filho and Rasmussen (1993); [e]Delesalle and Heubel (1972)

As shown in Figure 3.17 for the water/ethanol/KCl system it was found a good resemblance at the three different temperatures studied in this work and for all composition range. The systems with NaCl and KBr are only compared at 298.15 K, as shown in Figure 3.18, indicating that the agreement for NaCl salt is not so good. As a matter of fact, in the middle composition range it is possible to observe higher deviations although an analytical gravimetric technique was also used by Marcilla et al. (1995). However, it seems that the solubilities measured in this work are closer to the average curve.

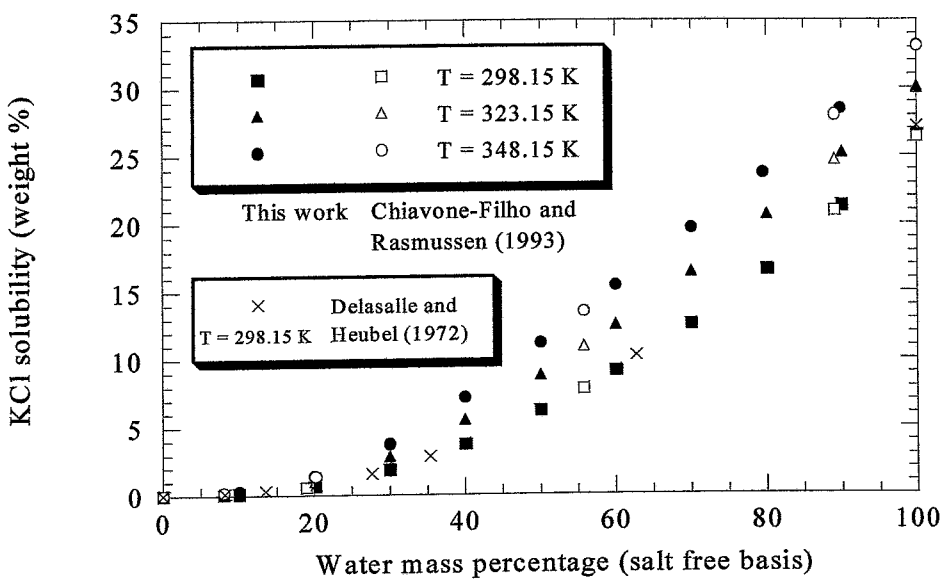

Figure 3.17 Comparison of water/ethanol/KCl system isotherms.

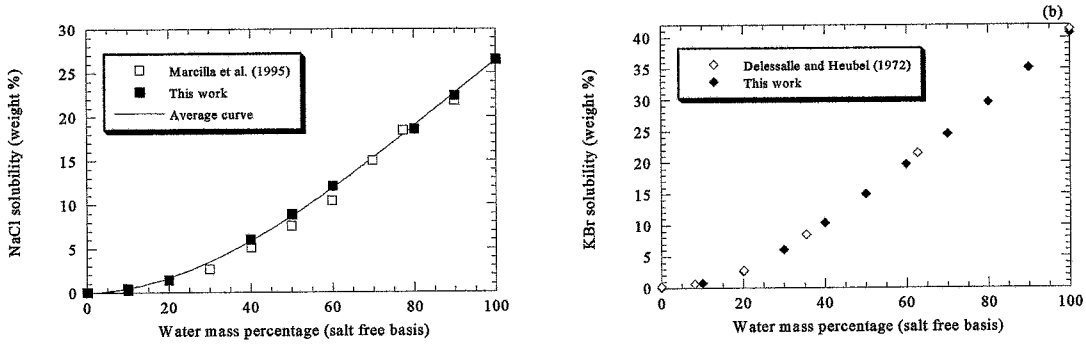

Figure 3.18 Comparison of salt solubility in water/ethanol mixtures at 298.15 K: (a) NaCl (b) KBr.

For the methanol/ethanol solvent mixtures the only data set found was for NaBr at 298.15 K. However, the values showed high inconsistency, in the pure solvents, and no comparison is presented.

3.5 Conclusions

The simple apparatus designed for the measurement of salt solubilities in mixed solvents using an analytical method proved to be very successful; high precision and accurate results were obtained and generally the solubilities are reproducible when compared to the values reported in the literature.

The systematized experimental study implemented in this work is an important contribution for the fulfilling of the great demanding of salt solubility in non-aqueous and mixed solvent systems; a high number of new experimental solubilities have been measured for the salts NaCl, KCl, NaBr, KBr, in the pure solvents water, methanol, ethanol, and in the mixed solvents water/methanol, water/ethanol and methanol/ethanol at different temperatures.

The number of experimental measured solubilities, temperature and composition ranges covered in the different studied systems, together with other experimental thermodynamic properties or equilibrium for this kind of systems allow the establishment of a large and reliable database, fundamental for the development of any thermodynamic model. This will be presented in the following chapter.

List of Symbols

n	number of experimental data points
s	standard deviation
x_i	experimental solubility of sample i
$\bar{x}$	arithmetical mean of n experimental results
w'	mass percentage in salt free basis
$wt\%$	mass percentage

Chapter 4

MODELLING OF SOLID-LIQUID EQUILIBRIUM

4. Modelling of Solid-Liquid Equilibrium

4.1 Introduction

The ability to correlate and/or predict phase equilibria is fundamental for the simulation of separation processes. Specifically, some examples supporting the interest for the study of solid-liquid equilibrium (SLE) in mixed solvents have already been given. Thus, in this chapter a new formulation is presented for the calculation of salt solubilities in pure and mixed solvents, as a function of the temperature and solvent composition. The formulation is based on the symmetric convention for the normalization of the activity coefficients for all species in solution and makes possible the direct access to the solubility product of the salt in terms of its thermodynamic properties. The new solubility data measured in this work and presented in chapter 3, as well as experimental information from the open literature are used to correlate the interaction parameters of the two models proposed here. One model combines the original UNIQUAC equation with a Pitzer-Debye-Hückel expression to take into account the long-range interaction forces; the other model only considers the short-range forces through the UNIQUAC equation with linear temperature dependent salt/solvent interaction parameters. Both models correlate satisfactorily the solubility data, although temperature and electrostatic effects are both very important in this type of equilibrium. Finally, some conclusions are drawn concerning the models versatility to represent other type of equilibrium data and prediction capabilities.

4.1.1 Previous Modelling Work

Generally, modelling processes with electrolytes is not routine and an easy task to perform, and problems that usually arise in the modelling of SLE are numerous (Perkyns and Pettitt, 1994; Liu and Watanasiri, 1999). Besides to the different concentration scales and standard states possible to adopt, the extreme complexity of the physical and chemical phenomena that might occur in the liquid phase, like solvation or association (Furter, 1992), the great lack of available and accurate data, and the broad range of the salt composition (from near zero up to the saturation), are the major restrictive factors for the establishment of an accurate model for SLE calculations.

Therefore, it is not surprising that, up to now, only a few works have been carried out in this area. Lorimer (1993) developed a method based on the unsymmetric convention for the normalization of the activity coefficients, which introduces enormous difficulties in the solubility calculations due to Gibbs energy of transfer that must be known. Also during 1993, Chiavone-Filho combined the UNIQUAC equation with temperature dependent water/ion parameters, with a Pitzer-Debye-Hückel expression to take into account, respectively, the short and long-range interaction forces. Since each system was correlated separately, the results were very satisfactory, with deviations between 1.2 and 7.4%. Finally, Kolker and de Pablo (1996a,b), without using any ternary data, predicted SLE in mixed solvents with a NRTL based model, achieving a reasonable agreement with the experimental data. The accuracy of the prediction varies from one system to another and the effect of temperature on the solubilities is not considered, since the study was only done at 298.15 K.

However, a systematic study, which is known to be fundamental nowadays, has not been tried in the above-mentioned works.

4.2 Model Development

The developed models to describe the SLE of salts in pure and mixed solvents are described in the following sections.

4.2.1 Fundamental Equation for Solid-Liquid Equilibrium

In section 2.2.5 it was pointed out the major difficulty for SLE calculations in mixed solvents. In fact, the common practice in electrolyte thermodynamics is the use of the unsymmetric convention for the ions, which for the representation of vapour-liquid equilibrium (VLE) does not introduce any difficulties, since the equilibrium criteria only involves the solvent species.

For SLE calculations, using this unsymmetric convention, a major difficulty arises from the fact that the salt standard chemical potential in the liquid phase, which depends on the mixed solvent composition, should be known. However, no suitable models for that property exist yet and so, to overcome that problem, a new formulation based on the symmetric convention for all species in solution and in the ionized mole fraction basis for the concentration scale is presented here.

Considering the solubleness of a salt $M_{\nu+}X_{\nu-}.nH_2O$ that completely dissociates, according to equation 4.1, into ν_+ cations M^{z+} with charge z_+, ν_- anions X^{z-} with charge z_-, and n water molecules:

$$M_{\nu+}X_{\nu-}.nH_2O(s) \leftrightarrow \nu_+M^{z+} + \nu_-X^{z-} + nH_2O \tag{4.1}$$

The SLE criterion states that the salt chemical potential in the solid phase must be equal to the sum of its constituent chemical potentials (μ):

$$\mu_{salt}(s) = \nu_+\mu_{M^{z+}} + \nu_-\mu_{X^{z-}} + n\mu_{H_2O} \tag{4.2}$$

Adopting pure liquid state at the system temperature and pressure as the standard state for all the components and using mole fraction (x) as the concentration scale, the chemical potentials of each salt constituent are expressed by equation 2.8, which combined with equation 2.9, may be written as:

$$\mu_i = \mu_i^\circ + RT\ln(f_i x_i) \tag{4.3}$$

In this last equation R is the ideal gas constant, T is the absolute temperature, f_i is the rational activity coefficient of species i, and superscript $\circ$ refers to the standard state adopted.

Applying this result to equation 4.2, and assuming the solid phase to be a pure salt, then its chemical potential is equal to the standard chemical potential in the solid phase $\mu_{salt}(s) = \mu^{\circ}_{salt}(s)$. It is then possible to write:

$$\mu^{\circ}_{salt}(s) = \mu^{\circ}_{salt}(l) + RT \ln(x_+^{\nu_+} f_+^{\nu_+} x_-^{\nu_-} f_-^{\nu_-} x_{H_2O}^{n} f_{H_2O}^{n}) \tag{4.4}$$

where f_+ and f_- are, respectively, the cation and anion, mole fraction scale activity coefficients; $\mu^{\circ}_{salt}(l)$ is the sum of the salt constituents standard chemical potentials.

The symmetric convention for the activity coefficients is adopted in this work, being the pure liquid at solution temperature and pressure the salt standard state. Even if the salts melt at a somewhat higher temperature, this supercooled liquid reference state is very useful since it makes accessible the solubility product of the salts. This procedure was successfully applied for the solubility of NaCl in water at temperatures well below the melting temperature (Pitzer and Simonson, 1986) and for several salts in water at low temperatures (Kolker, 1992).

Rosen (1979) has pointed out that the salt mole fraction (x_{salt}) on ionized basis (Pitzer, 1980) is properly applied to this standard state and can be related to the ions mole fractions by:

$$x_i = \frac{\nu_i}{\nu} x_{salt} \tag{4.5}$$

where ν is the sum of the cation and anion stoichiometric coefficients.

At this point, an explanation is needed concerning the measure of the composition of the salt components. As already mentioned in chapter 2, it is not possible to use the molality scale for the salt standard state used here because molality becomes infinite for the pure salt. Also, the sum of mole fractions should be unity, hence the number of ions in the salt is included in the definition of its mole fraction in contrast to the common practice for the molality of the salt. Therefore, the composition of the system in terms of the ions and solvents is calculated using equation 2.3, whereas the mole fraction of salt on ionized basis is given by:

$$x_{salt} = \frac{\nu m_{salt}}{\nu m_{salt} + \sum_{m=1}^{N_{solv}} n_m} \tag{4.6}$$

where n_{salt} is the number of moles of salt, n_m is the number of molecules of the solvent m and N_{solv} is the total number of solvents in solution.

Combining equations 4.4 and 4.5:

$$\mu^{\circ}_{salt}(s) = \mu^{\circ}_{salt}(l) + \nu RT \ln\left(\frac{Qf_{\pm}x_{salt}}{\nu}\right) + nRT \ln a_{H_2O} \tag{4.7}$$

The Q coefficient and the salt mean ionic activity coefficient ($f_{\pm}$) are equal to:

$$Q^{\nu} = \nu_{+}^{\nu_{+}}\nu_{-}^{\nu_{-}} \tag{4.8}$$

$$f_{\pm}^{\nu} = f_{+}^{\nu_{+}} f_{-}^{\nu_{-}} \tag{4.9}$$

Taking into consideration the salt solubility product definition (K_{salt}), a relation for this equilibrium constant is easily obtained from equation 4.7:

$$K_{salt} = \exp\left(\frac{\mu^{\circ}_{salt}(s) - \mu^{\circ}_{salt}(l)}{RT}\right) = \left(\frac{Qf_{\pm}x_{salt}}{\nu}\right)^{\nu} a^{n}_{H_2O} \tag{4.10}$$

Therefore, the salt solubility calculation is possible if an activity coefficient model and K_{salt} are available.

In order to obtain K_{salt}, a thermodynamic cycle was idealized between the pure solid and liquid salt phase states which, after some assumptions, leads to the following expression (Prausnitz et al., 1998):

$$K_{salt} = \exp\left[\frac{\Delta H_f}{R}\left(\frac{1}{T_f} - \frac{1}{T}\right) + \frac{\Delta c_{pf}}{R}\left(\frac{T_f}{T} - 1 + \ln\frac{T}{T_f}\right)\right] \tag{4.11}$$

As already stated, the solubility product is related to some thermodynamic properties of the salt such as the melting temperature (T_f), the enthalpy of fusion (ΔH_f) at T_f, and the change of heat capacity (ΔC_{pf}), between the liquid and solid state also at T_f, defined by:

$$\Delta C_{pf} = C_p(T_f)_{liquid} - C_p(T_f)_{solid} \tag{4.12}$$

Equation 4.11 has been widely applied for the representation of solid-liquid equilibrium of non-electrolyte systems, namely of binary hydrocarbon mixtures (Lohmann et al., 1997), hydrocarbons in mixed solvents (Prausnitz et al., 1998; Zhu et al., 1999), and sugars in pure and mixed solvents (Peres and Macedo, 1996; 1997a,b,c). Kolker (1991; 1992) has been well succeeded in the calculation of salt solubility in water, using this procedure, but has pointed out the high sensitivity on the heat of fusion for the obtained results.

Concerning the activity coefficient models the two approaches proposed are discussed in sections 4.2.2 and 4.2.3.

4.2.2 UNIQUAC + Pitzer-Debye-Hückel Model

From the study presented in chapter 2, it was possible to conclude that the best available models to represent phase equilibria in mixed solvents electrolyte systems are still the semi-empirical models. Thus, in this work a semi-empirical model based on the assumption that the symmetric molar excess Gibbs function (G^E) of the system on mole fraction basis is a linear combination of two terms is proposed:

$$G^E = G^E_{UNIQUAC} + G^E_{PDH} \tag{4.13}$$

The original UNIQUAC model has been chosen due to the accurate results obtained for the description of the short-range forces in non-electrolyte systems (Abrams and Prausnitz, 1975; Prausnitz et al, 1998), as well as for mixed solvent electrolyte systems (Sander et al, 1986; Macedo et al., 1991; Li et al., 1994), as was discussed in chapter 2. Furthermore, it is possible to extend it to multicomponent systems or to a group-contribution method.

To account for the long-range forces a Pitzer-Debye-Hückel (PDH) equation is used. In fact, Pitzer (1980), Pitzer and Simonson (1986) and Simonson and Pitzer (1986) have developed proper equations to calculate the activity coefficients of all species in the symmetric convention and ionized basis mole fraction scale, as used in this work. Though the published studies concerned only aqueous systems, it is suggested by those authors the study, with adequate modifications, of the capabilities of this model for mixed solvent systems.

From equation 4.13 the rational symmetric activity coefficient for any species, ion or solvent, can be derived as:

$$\ln f_i = \ln f_i^{UNIQUAC} + \ln f_i^{PDH} \tag{4.14}$$

The UNIQUAC model (Abrams and Prausnitz, 1975) calculates the activity coefficient of species i ($f_i^{UNIQUAC}$) in the mole fraction scale and symmetric convention, according to:

$$\ln f_i^{UNIQUAC} = \ln f_i^C + \ln f_i^R \tag{4.15}$$

The combinatorial term f_i^C, representing the differences in size and shape of the species in the system, is the same as in the original equation:

$$\ln f_i^C = \ln \frac{\phi_i}{x_i} + 5q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^{N_{spec}} x_j l_j \tag{4.16}$$

where,

$$l_i = 5(r_i - q_i) - (r_i - 1) \tag{4.17}$$

The volume fraction (ϕ_i) and surface area fraction (θ_i) of component i are calculated with the relationships:

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \tag{4.18}$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{4.19}$$

In these equations j refers to the total number of species in the solution, and pure molecular or ion parameters r_i and q_i are, respectively, measures of molecular van der Waals volumes and molecular surface areas.

The residual term f_i^R, takes the short-range molecular energetic interactions into account, and is expressed as:

$$\ln f_i^R = q_i \left[1 - \ln\left(\sum_j \theta_j \tau_{ji} \right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right] \tag{4.20}$$

The summations refer to the total number of molecules in the solution, and the parameter τ is given by:

$$\tau_{ij} = \exp\left(-\frac{a_{ij}}{T}\right) \tag{4.21}$$

where a_{ij} is the UNIQUAC interaction parameter between the species i and j.

Since the symmetric convention is used for all the components, a conversion is necessary when using the UNIQUAC model. In fact, for the salt, as the ion activity coefficients are first evaluated, the calculation of their activity coefficients in a pure salt system should be performed. The conversion can be expressed as:

$$\ln f_i(\underline{x},T) = \ln f_i^{UNIQUAC}(\underline{x},T) - \ln f_i^{UNIQUAC}\left(\frac{\nu_i}{\nu},T\right) \tag{4.22}$$

This last equation requires some attention. For an ionic species i, the normalized activity coefficient, f_i, will be equal to one when x_{salt} is unity or in terms of ions composition when x_i is equal to the ratio ν_i/ν. So, for a multicomponent mixture with a mole fraction vector $\underline{x}$ and temperature T, the ion activity coefficient should be determined by equation 4.22.

The PDH contribution presented in equation 4.14 is given as:

$$\ln f_i^{PDH} = -z_i^2 A_{DH,x}\left[\frac{2}{b}\ln\left(\frac{1+b\sqrt{I_x}}{1+b\sqrt{I_x^{\nabla}}}\right)+\sqrt{I_x}\frac{1-I_x/I_x^{\nabla}}{1+b\sqrt{I_x}}\right] \tag{4.23}$$

where,

$$A_{DH,x} = \frac{1}{3}\frac{\sqrt{2*N_A}}{8\pi}\left(\frac{e^2}{\varepsilon_\circ k}\right)^{1.5}\frac{\rho_\circ^{0.5}}{(\varepsilon T)^{1.5}} \tag{4.24}$$

$$I_x = 0.5\sum_{l=1}^{N_{ion}} z_l^2 x_l \tag{4.25}$$

For electrolytes, like the ones studied in this work, with unitary charge for each ion:

$$I_x^{\nabla} = z_i^2/2 \tag{4.26}$$

In equations 4.23 and 4.24 b is a parameter related to the closest approach of the ions, N_A is Avogrado's number, e is the electronic charge, $\varepsilon_\circ$ is the vacuum permittivity, k is the Boltzmann constant, which are all given in section 2.3.1. Finally, $\rho_\circ$ and ε are, respectively, the density ($molcm^{-3}$) and the dielectric constant of the solvent.

For a solvent m, the charge number is zero and equation 4.23 reduces to:

$$\ln f_m^{PDH} = A_{DH,x} \frac{2I_x\sqrt{I_x}}{1+b\sqrt{I_x}} \tag{4.27}$$

It should be noticed that expressions 4.23 and 4.27 are obtained by proper differentiation of the excess Gibbs energy, G_{PDH}^E, which in the original paper was developed for single solvent systems. Similarly to Koh et al. (1985), Chen and Evans (1986), and Achard et al. (1994), in this work, the differentiation of the parameter $A_{DH,x}$ which is solvent composition dependent through the density and the dielectric constant of the solvent has been neglected. The values of that parameter are, however, evaluated as a function of the solvent composition as will be shown in section 4.2.2.1.

The use of this activity coefficient model requires:

- The temperature and composition dependency of the Pitzer-Debye-Hückel parameter $A_{DH,x}$ according to equation 4.24, and the distance of closest approach parameter, b.
- The structural parameters r_i and q_i, of solvents and ions, and finally the interaction parameters between the different molecules or ions present in the solution.

4.2.2.1 Pitzer-Debye-Hückel Parameters

The temperature and composition dependency of the $A_{DH,x}$ parameter is considered via equation 4.24, using different methods to estimate the density and the dielectric constant of the solvent.

(a) Density of the pure and mixed solvent mixtures

The molar density of the mixed solvent ρ_{ms} ($kmolm^{-3}$) can be calculated based on the density of its constituents pure solvents densities ($\rho_m^{\bullet}$), which may be found on the DIPPR Tables (1984), according to the empirical equation:

$$\rho_{ms} = \frac{1}{\sum_{m=1}^{N_{solv}} x_m' / \rho_m^{\bullet}} \tag{4.28}$$

where $\rho_m^{\bullet}$ is also given in $kmolm^{-3}$, and x_m' is the salt-free mole fraction of solvent m in the liquid phase.

(b) Dielectric constant of the pure and mixed solvent mixtures

The dielectric constant of a solvent mixture ε_{ms} is obtained from the pure solvent values (ε_m) given by Maryott and Smith (1951). For a binary mixed solvent mixture, constituted by solvents *1* and *2*, the Oster's mixing rule (Franks, 1973) is adopted:

$$\varepsilon_{ms} = \varepsilon_1 + \left[\frac{(\varepsilon_2 - 1)(2\varepsilon_2 - 1)}{2\varepsilon_2} - (\varepsilon_1 - 1) \right] \varphi_2' \tag{4.29}$$

where φ_2' is the solvent salt free basis volumetric fraction, defined for any solvent m by:

$$\varphi_m' = \frac{x_m'}{\rho_m^{\bullet}} \rho_{ms} \tag{4.30}$$

For a mixture with more than two solvents the dielectric constant of the mixed solvent is estimated according to (Li et al., 1994):

$$\varepsilon_{ms} = \sum_{m=1}^{N_{solv}} \varepsilon_m \varphi_m' \tag{4.31}$$

The expressions used in this work to calculate pure solvent properties like density and dielectric constants are given in Appendix B. A comparison between the experimental results of the dielectric constant of mixed solvent mixtures and the predictions using the Oster's mixing rule is also shown in this appendix.

The parameter b depends on the short-range model used and on the solvent composition, and may be considered as a parameter to estimate in the range 8 to 15 (Pitzer, 1980) during the experimental data fitting. However, in this work a constant value of 14.9 was used. This value was also set by several authors for the study of phase equilibria in aqueous (Pitzer, 1980; Simonson and Pitzer, 1986) and mixed solvent electrolyte systems with the NRTL equation (Chen and Evans, 1986; Barata and Serrano, 1997). Achard et al. (1994), using the UNIFAC model by Larsen et al. (1987), have given a slightly higher value for this parameter ($b = 17.1$).

4.2.2.2 Structural Parameters

The structural parameters r_i and q_i are the measures of the van der Waals volumes and surface areas, respectively. For molecules and organic ions, they are usually estimated with the method proposed by Bondi (1968), and for the other ions based on the molecular size of the ions. However, the very small values of the ionic radii for the cations lead to q values in the range 0.1-0.5. Sander et al. (1986) have concluded that values of this magnitude reduce the fitting capabilities of the UNIQUAC equation, and therefore r and q can be treated as adjustable parameters.

In order to reduce the number of parameters to estimate, in this work, the fixed values used by Macedo et al. (1990), Kikic et al. (1991) with, respectively, the UNIQUAC and UNIFAC models for VLE in mixed solvent are applied. The values of the structural parameters of the solvents and ions are given in Table 4.1.

Table 4.1 UNIQUAC volume (r_i) and surface (q_i) area parameters.

	Water	Methanol	Ethanol	Na^+	K^+	Cl^-	Br^-
r_i	0.92	1.4311	2.1055	3.0	3.0	0.9861	1.2331
q_i	1.40	1.4322	1.9720	3.0	3.0	0.9917	1.1510

4.2.3 UNIQUAC Model

In order to test the capabilities of the UNIQUAC model and to perform comparisons with the previous model, the use of the UNIQUAC equation alone, considering the salt in the molecular form is also proposed.

Thus, for this case the rational symmetric activity coefficient for any species, salt or solvent, can be derived as:

$$\ln f_i = \ln f_i^{UNIQUAC} \tag{4.32}$$

The equations used to calculate $f_i^{UNIQUAC}$ already presented for the UNIQUAC + PDH model still hold for this case. The only change is the introduction of a temperature dependency for the interaction parameters between the salt (l) and the solvent (m) in accordance to:

$$a_{lm} = a_{lm}^{\circ} + a_{lm}^{t}(T - 298.15) \tag{4.33}$$

and:

$$a_{ml} = a_{ml}^{\circ} + a_{ml}^{t}(T - 298.15) \tag{4.34}$$

where the superscripts $\circ$ and t refer, respectively, to the reference interaction parameter and to the temperature dependent parameter. This linear temperature dependency is applied only if the temperature interval of the available experimental data is at least 50 K.

The structural parameters r_i and q_i, of solvents and salts, and finally the interaction parameters between the different molecules present in the solution are the only requirements for the application of this model. While for the solvents the structural parameters are the same as presented in Table 4.1, for the salts they were obtained from Dahl and Macedo (1992). They are shown in Table 4.2.

Table 4.2 UNIQUAC volume (r_l) and surface (q_l) area parameters for the salts.

	NaCl	KCl	NaBr	KBr
r_l	5.9861	5.9861	6.2331	6.2331
q_l	5.9917	5.9917	6.1510	6.1510

4.3 Parameter Estimation

To estimate the energy interaction parameters for the two proposed models, a modified Levenberg-Marquardt method (Levenberg, 1944; Marquardt, 1963) was used to minimize the following objective function (OBJ):

$$OBJ = \sum_{p=1}^{N_{SLE}} \omega_d \left(\frac{x_{salt,p}^{calc} - x_{salt,p}^{exp}}{x_{salt,p}^{exp}} \right)^2 + \sum_{p=1}^{N_{VLE}} \omega_d \left(\frac{\phi_p^{calc} - \phi_p^{exp}}{\phi_p^{exp}} \right)^2 \tag{4.35}$$

where $calc$ and exp mean the experimental and calculated values according to the model, N_{SLE} and N_{VLE} are, respectively, the total number of experimental SLE and VLE data points, ϕ is the osmotic coefficient, ω_d is a weighting factor for data set number d, and p refers to the experimental point.

To calculate the salt solubility using the developed methodology it turned out to be useful rewrite equation 4.10 in a more explicit way:

$$x_{salt}^{calc} = \frac{\nu}{Qf_{\pm}} \sqrt[\nu]{\frac{K_{salt}}{a_{H_2O}^n}} \tag{4.36}$$

As can be seen from equation 4.36, the salt solubility calculation involves an iterative procedure for the system composition, since it depends on the activity coefficients, which in turn are composition dependent. To be able to perform the calculations, the thermodynamic properties of the studied salts, that must be known, were found in JANAF thermochemical tables (Chase Jr. et al., 1985) and are listed in Table 4.3.

Table 4.3 Calorimetric data of the studied salts.

Salt	$T_f(K)$	$\Delta H_f(calmol^{-1})$	$\Delta C_{pf}(calmol^{-1}K^{-1})$
NaCl	1073.8	6730	0.788
KCl	1044.0	6282	1.030
NaBr	1020.0	6240	0.240
KBr	1007.0	6100	0.360

4.3.1 Water/Salt Systems

4.3.1.1 Database

An extensive and reliable database on salt solubility and osmotic coefficient data was built to allow the estimation of the relevant energy interaction parameters needed to represent the water/salt systems. The solubility data used includes the experimental results obtained in this work, as well as those selected from the open literature, applying the coherence tests already explained in section 3.2.1 to accept a specific data set.

Concerning the experimental osmotic coefficients, they were, whenever possible, recalculated with the aid of more recently published data of the electrolytes used as a standard (Hamer and Wu, 1972; Clark and Glew, 1985) according to:

$$\phi_{salt} = \phi_{std}\left(\frac{\nu_{std} m_{std}}{\nu_{salt} m_{salt}}\right) \tag{4.37}$$

In equation 4.37 m is the molality of the salts in the equilibrium and subscript *std* refers to the standard electrolyte.

Relevant information about the experimental data collected is shown in Table 4.4.

4.3.1.2 New UNIQUAC Interaction Parameters

The objective function for simultaneous correlation of SLE and VLE data was defined by equation 4.35.

To fit the 737 data points selected, major relevance has been given to the salt solubility data so that the weighting factors ω_d have been set equal to 1 for that type of data, and between 0.1 and 0.3 for the osmotic coefficients. This was done because the main purpose of this work is the correlation and prediction of salt solubilities in mixed solvents. Accordingly, for the experimental VLE data used in the parameter estimation, for which the number of experimental data points is much higher than for the solubilities, a low weight factor was used.

Table 4.4 *Representation of the experimental data collected in terms of the number of experimental data points, temperature range and salt concentration range.*

Salt	Data Type	Number of Data Points	Temperature Range (K)	Concentration Range (*wt%*)
NaCl	Solubility[a]	76	273.15 – 373.15	26.27 – 28.15
	ϕ[b]	242	273.15 – 373.15	0 – 28.08
KCl	Solubility[c]	72	273.15 – 373.15	21.60 – 36.20
	ϕ[d]	71	298.15 – 372.75	0 – 27.83
NaBr	Solubility[e]	34	273.15 – 373.15	44.50 – 54.50
	ϕ[f]	98	293.02 – 362.07	0 – 48.08
KBr	Solubility[g]	26	273.15 – 373.15	34.90 – 51.00
	ϕ[h]	118	298.15 – 373.15	0 – 39.56

[a]Linke and Seidell (1958), Stephen and Stephen (1963), Clark and Glew (1985), Farelo et al. (1993); [b]Clark and Glew (1985); [c]Linke and Seidell (1958), Stephen and Stephen (1963), Chiavone-Filho and Rasmussen (1993), Farelo et al. (1993), Zhang et al. (1998); [d]Patterson et al. (1960), Hellams et al. (1965), Hamer and Wu (1972), Davis et al. (1985); [e]Linke and Seidell (1958); [f]Penciner and Marcus (1965), Hamer and Wu (1972), Jakli and Van Hook (1972), Patil et al. (1991), Rard and Archer (1995); [g]Linke and Seidell (1958), Stephen and Stephen (1963), Chiavone-Filho and Rasmussen (1993); [h]Robinson and Stokes (1970), Hamer and Wu (1972).

Sixteen parameters were estimated for each model proposed here: four parameters ($a^{\circ}_{water,salt}$, $a^{\circ}_{salt,water}$, $a^{t}_{water,salt}$, $a^{t}_{salt,water}$) per system for the UNIQUAC model, and for the UNIQUAC + PDH model, all data were used simultaneously to estimate 8 water/ion parameters (a_{water,Na^+}, a_{water,K^+}, a_{water,Cl^-}, a_{water,Br^-}, $a_{Na^+,water}$, $a_{K^+,water}$, $a_{Cl^-,water}$, $a_{Br^-,water}$) and 8 cation/anion parameters (a_{Na^+,Cl^-}, a_{K^+,Cl^-}, a_{Na^+,Br^-}, a_{K^+,Br^-}, a_{Cl^-,Na^+}, a_{Cl^-,K^+}, a_{Br^-,Na^+}, a_{Br^-,K^+}).

The new estimated interaction parameters for the UNIQUAC and UNIQUAC + PDH models are listed, respectively, in Tables 4.5 and 4.6.

Table 4.5 New interaction parameters a° (K) and a^{t} for the UNIQUAC model.

	H_2O	$NaCl$	KCl	$NaBr$	KBr
H_2O	0.0	-290.3 0.6166^{t}	-137.0 -0.0581^{t}	-474.3 -1.018^{t}	-131.5 0.7010^{t}
$NaCl$	281.5 0.8105^{t}	0.0	n. a.	n. a.	n. a.
KCl	127.9 0.9031^{t}	n. a.	0.0	n. a.	n. a.
$NaBr$	1002 5.121^{t}	n. a.	n. a.	0.0	n. a.
KBr	66.67 -0.2137^{t}	n. a.	n. a.	n. a.	0.0

^{t}According to equations 4.33 and 4.34; n. a.: not available.

Table 4.6 New interaction parameters (K) for the UNIQUAC + PDH model.

	H_2O	Na^{+}	K^{+}	Cl^{-}	Br^{-}
H_2O	0.0	-209.5	-1095	-247.8	-282.1
Na^{+}	58560	0.0	n. a.	-2.380	0.3380
K^{+}	-89.18	n. a.	0.0	320.5	307.3
Cl^{-}	-602.2	24.84	-1981	0.0	n. a.
Br^{-}	-616.8	12320	-1998	n. a.	0.0

n. a.: not available.

At this point some comments should be given concerning the NaBr/water system. This particular salt forms a dihydrated solid phase at temperatures lower than 323.98 K (Rard and Archer, 1995). However, the calorimetric data found in the literature, given in Table 4.3, are only for non-hydrated salts, and so, can not be used to calculate the solubility product of $NaBr.2H_2O$.

Several alternatives can be adopted to overcome this problem. The most common would be the estimation of the temperature dependency of the term $\mu^{\circ}_{salt}(s) - \mu^{\circ}_{salt}(l)$, expressed in equation 4.10, using solubility data, but the reduced number of experimental data points available and the narrow temperature range studied are restrictive factors to apply this methodology.

Avoiding also the introduction of new parameters to be estimated, a different procedure was employed in this work. It comes from the fact that the calculation of the salt solubility either using K_{NaBr} or $K_{NaBr.2H_2O}$, via equation 4.36, should be the same at the invariant point. In this way, the following equation was derived:

$$K_{NaBr.2H_2O} = a^2_{H_2O} K_{NaBr} \tag{4.38}$$

where a_{H_2O} is the water activity at the invariant point.

4.3.2 Organic Solvent/Salt and Ternary Systems

4.3.2.1 Database

The data sets compiled from the literature and the experimental solubilities obtained in this work were included to establish a reliable and extensive database on salt solubility in non-aqueous and mixed solvent systems. These are used in the estimation of the relevant energy interaction parameters needed to represent those systems. Information about the experimental data collected is shown in Table 4.7.

It should be mentioned that, as a matter of convenience, the experimental data for the solubility of salts in pure methanol and ethanol were included, respectively, in the water/methanol and water/ethanol mixed solvent systems.

Table 4.7 *Representation of the experimental data collected in terms of the number of experimental data points, temperature range and salt concentration range*[*].

Mixed Solvent	NaCl	KCl	NaBr	KBr
Water	40 (19)	53 (19)	30 (23)	43 (23)
+		298.15 – 333.15		
Methanol[a]	1.22 – 26.29	0.43 – 25.87	13.94 – 46.25	2.04 - 40.66
Water	94 (22)	87 (30)	34 (30)	64 (30)
+	273.15 – 348.15		298.15 – 348.15	
Ethanol[b]	0.07 – 26.06	0.02 – 28.45	2.30 – 50.89	0.14 – 43.93
Methanol	8 (8)	8 (8)	18 (18)	8 (8)
+		298.15 – 323.15		
Ethanol	0.14 – 0.89	0.07 – 0.42	3.26 – 13.57	0.29 – 1.72

[*] For each system the first row is the number of experimental data points, the second is the temperature range (K) and the third is the salt concentration range (*wt%*). In brackets the number of data points obtained in this work are indicated; [a] Stephen and Stephen (1964), Malahias and Popovych (1982), Stenger (1996); [b] Stephen and Stephen (1964), Delasalle and Heubel (1972), Chiavone-Filho and Rasmussen (1993), Marcilla et al. (1995).

4.3.2.2 New UNIQUAC Interaction Parameters

The 166 experimental solubility data points for water/methanol/salt systems were fitted using the same objective function (equation 4.35) as described before. However, no experimental VLE information was included in the database, since it turned out during the minimization process that it was difficult to represent simultaneously, with high accuracy, both types of data.

Once more, the same number of parameters (10) were estimated for each of the two models proposed: two parameters ($a^{\circ}_{methanol,salt}$, $a^{\circ}_{salt,methanol}$) per system for the UNIQUAC model, summing 8 parameters, and for the UNIQUAC + PDH model, 8 methanol/ion parameters ($a_{methanol,Na^+}$, $a_{methanol,K^+}$, $a_{methanol,Cl^-}$, $a_{methanol,Br^-}$, $a_{Na^+,methanol}$, $a_{K^+,methanol}$, $a_{Cl^-,methanol}$, $a_{Br^-,methanol}$).

Additionally, the two interaction parameters between the solvents water and methanol were also estimated.

It should be stressed that, in this case, no temperature dependency on the UNIQUAC model parameters was introduced, because of the narrow temperature range of the available experimental data.

The other relevant parameters to represent the mixed solvent systems involving ethanol were obtained regressing the 321 data points collected for the water/ethanol and methanol/ethanol mixed solvents: besides the four interaction parameters between the solvents ($a_{water,ethanol}$, $a_{ethanol,water}$, $a_{methanol,ethanol}$, $a_{ethanol,methanol}$) needed for both models, 4 interaction parameters for each salt ($a^{\circ}_{ethanol,salt}$, $a^{\circ}_{salt,ethanol}$, $a^{t}_{ethanol,salt}$, $a^{t}_{salt,ethanol}$) were also estimated for the UNIQUAC model, and 8 ethanol/ion parameters ($a_{ethanol,Na^+}$, $a_{ethanol,K^+}$, $a_{ethanol,Cl^-}$, $a_{ethanol,Br^-}$, $a_{Na^+,ethanol}$, $a_{K^+,ethanol}$, $a_{Cl^-,ethanol}$, $a_{Br^-,ethanol}$) were regressed for the UNIQUAC + PDH model.

A difference in terms of the number of parameters arises here. While for the UNIQUAC model 20 parameters were calculated, for the UNIQUAC + PDH it was only necessary to estimate 12 parameters.

The new estimated interaction parameters for the UNIQUAC and the UNIQUAC + PDH models are listed, respectively, in Tables 4.8 and 4.9.

4.4 Results and Discussion

The quality of the correlations and a comparison between the performance of the proposed models can be made by calculating the absolute average deviation (*AAD*):

$$AAD(\%) = \frac{100}{N_{data}} \sum_{p=1}^{N_{data}} \left| \frac{y_p^{calc} - y_p^{\exp}}{y_p^{\exp}} \right| \tag{4.39}$$

where y represents the thermodynamic property under study, the salt solubility or the osmotic coefficient, and N_{data} is the total number of experimental points for each property.

Table 4.8 New interaction parameters a° (K) and a^t for the UNIQUAC model.

	H_2O	Methanol	Ethanol	NaCl	KCl	NaBr	KBr
H_2O	0.0	-1114	-201.9	**a**			
Methanol	-227.4	0.0	-98.59	-119.8	-59.28	-262.4	-124.5
Ethanol	-1.315	420.6	0.0	-70.33 0.3240^t	106.6 2.240^t	-203.0 -0.1076^t	-68.28 -0.1284^t
NaCl	**a**	725.8	8911 -146.9^t	**a**			
KCl		896.3	278.4 -2.366^t				
NaBr		824.0	842.6 18.48^t				
KBr		1404	2599 -0.2028^t				

^{t}According to equations 4.33 and 4.34; **a**: already given in Table 4.5.

Table 4.9 New interaction parameters (K) for the UNIQUAC + PDH model.

	H_2O	Methanol	Ethanol	Na^+	K^+	Cl^-	Br^-
H_2O	0.0	-66.76	-327.4	**a**			
Methanol	-204.9	0.0	-556.7	-134.5	-1524	-402.4	-398.8
Ethanol	-33.52	526.9	0.0	-68.41	-1388	699.7	778.3
Na^+	**a**	287.4	554.4	**a**			
K^+		1336	8442				
Cl^-		10770	-261.7				
Br^-		-113.7	-487.4				

a: already given in Table 4.6.

4.4.1 Water/Salt Systems

Table 4.10 summarizes the *AAD* values obtained in the correlation of both salt solubility and osmotic coefficients with the UNIQUAC and the UNIQUAC + PDH models. The data used is summarized in Table 4.4.

Table 4.10 *AAD percentage values for water/salt systems in the correlation of salt solubility and osmotic coefficients.*

Salt	Data Type	UNIQUAC	UNIQUAC + PDH
NaCl	Solubility	0.44	3.39
	ϕ	10.39	8.26
KCl	Solubility	2.02	2.59
	ϕ	10.54	2.71
NaBr	Solubility	2.30	4.10
	ϕ	14.20	8.23
KBr	Solubility	2.22	2.73
	ϕ	12.20	3.79
Average	Solubility	1.51	3.15
	ϕ	11.52	6.51

From the results shown in Table 4.10, it is possible to conclude that while the UNIQUAC model is superior in the representation of salt solubility, the UNIQUAC + PDH model is more accurate for the correlation of osmotic coefficient data. This was, in some way, expected: the UNIQUAC model has 4 specific parameters for each salt, and the temperature influence is considered directly through the a^t parameters, although for the UNIQUAC + PDH model the temperature influence is only considered in the change of the solvent dielectric constant and the model has only two specific interaction parameters (anion/cation and cation/anion) for each salt.

On the other hand, the importance of a Debye-Hückel type expression in the representation of the electrostatic forces in electrolyte systems is completely shown. For very diluted solutions these forces are dominant (Robinson and Stokes, 1970; Prausnitz et al., 1998) and the UNIQUAC + PDH model can, as shown in Figure 4.1, accurately represent the osmotic coefficients in that concentration region.

Despite that a rigorous and simultaneous description of both properties is very difficult to obtain with these models, which is possible using for instance the model by Pitzer (Pitzer, 1973; Pitzer and Mayorga, 1973; Lima and Pitzer, 1983; Farelo et al., 1993), they have the very important characteristic, essential in this work, that is their potentiality of being easily extended to mixed solvent systems. Nevertheless, to represent the solubility of mixed electrolytes in water Lima and Pitzer (1983) and Farelo et al. (1993) needed to use equations, for the second and third virial coefficients, with a high number of empirical parameters to be able to describe their temperature dependency.

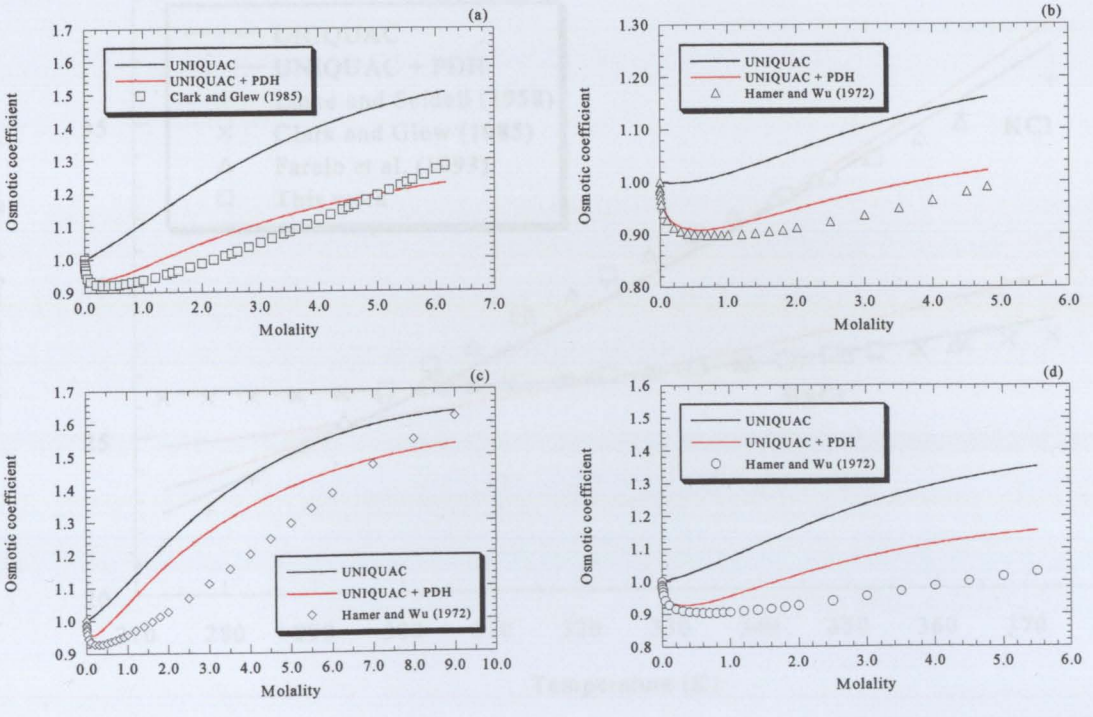

Figure 4.1 *Calculated and experimental osmotic coefficients in water/salt systems at 298.15 K: (a) NaCl (b) KCl (c) NaBr (d) KBr.*

In Figures 4.2 and 4.3 the experimental solubilities of the salts studied in this work are compared with those calculated with the models. Generally, the results are very acceptable, but differences between the UNIQUAC and UNIQUAC + PDH models performances, like indicated by the *AAD* values given in Table 4.10, are perceptible for the water/NaCl and water/NaBr systems. Moreover, the UNIQUAC model is better for the description of the solid phase transition.

In fact, while the water/NaCl system presents a slight dependency on the temperature, the water/NaBr system has a strong dependency up to 323.98 K and beyond this value, a little influence is observed. It seems that the common interaction parameters between water and the sodium ion can not contribute in the best way to follow those different behaviours, in completely accordance to the greater deviations also achieved in the correlation of the osmotic coefficients. It should be mentioned that Rard and Archer (1995), apart to the parameters used in the model by Pitzer, estimated more four parameters to represent the solubility for the water/NaBr system. This is an evidence for the difficulties in obtaining good correlation results for the representation of the solubility behaviour in electrolyte systems.

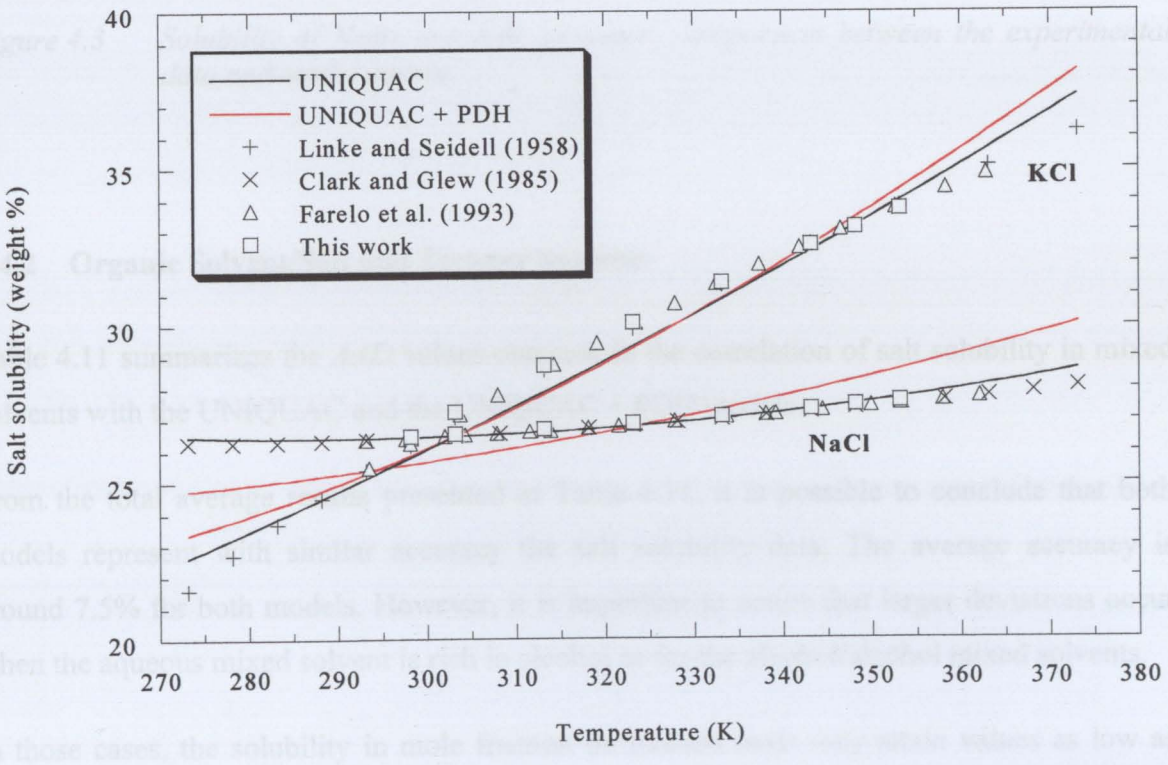

Figure 4.2 *Solubility of NaCl and KCl in water: comparison between the experimental data and model curves.*

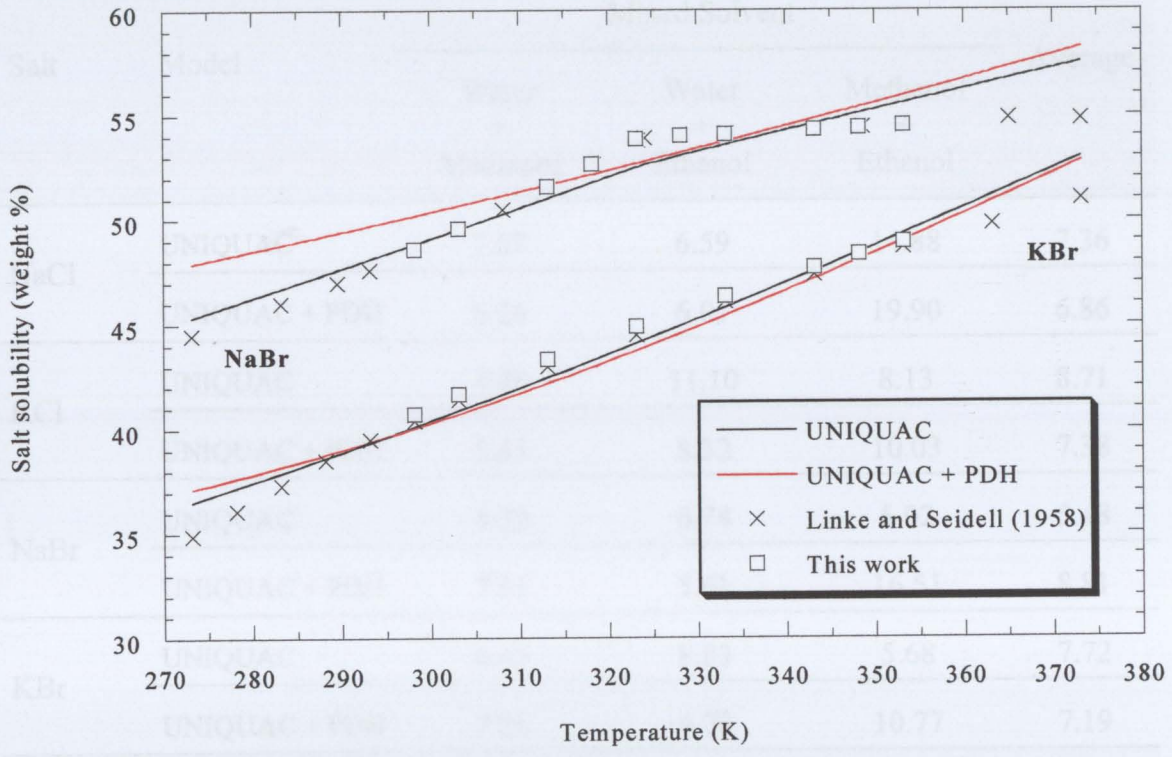

Figure 4.3 *Solubility of NaBr and KBr in water: comparison between the experimental data and model curves.*

4.4.2 Organic Solvent/Salt and Ternary Systems

Table 4.11 summarizes the *AAD* values obtained in the correlation of salt solubility in mixed solvents with the UNIQUAC and the UNIQUAC + PDH models.

From the total average results presented in Table 4.11, it is possible to conclude that both models represent with similar accuracy the salt solubility data. The average accuracy is around 7.5% for both models. However, it is important to notice that larger deviations occur when the aqueous mixed solvent is rich in alcohol or for the alcohol/alcohol mixed solvents.

In those cases, the solubility in mole fraction on ionized basis may attain values as low as 0.0004 (solubility of KCl in ethanol at 298.15 K), and a very small change for the calculated value gives rise to a very high percentage deviation.

Table 4.11 AAD percentage values for the correlation of salt solubility in mixed solvents.

Salt	Model	Mixed Solvent			Average
		Water + Methanol	Water + Ethanol	Methanol + Ethanol	
NaCl	UNIQUAC	7.67	6.59	14.88	7.36
	UNIQUAC + PDH	6.26	6.01	19.90	6.86
KCl	UNIQUAC	4.88	11.10	8.13	8.71
	UNIQUAC + PDH	5.45	8.32	10.03	7.38
NaBr	UNIQUAC	4.32	6.74	5.02	5.48
	UNIQUAC + PDH	7.81	5.61	16.51	8.81
KBr	UNIQUAC	6.45	8.83	5.68	7.72
	UNIQUAC + PDH	7.26	6.70	10.77	7.19
Average	UNIQUAC	5.86	8.53	7.62	7.54
	UNIQUAC + PDH	6.54	6.84	14.82	7.42

Figures 4.4 to 4.7 compare, for water/methanol mixed solvent, the experimental solubility of each salt with the calculated values with the models, at the two different temperatures studied in this work.

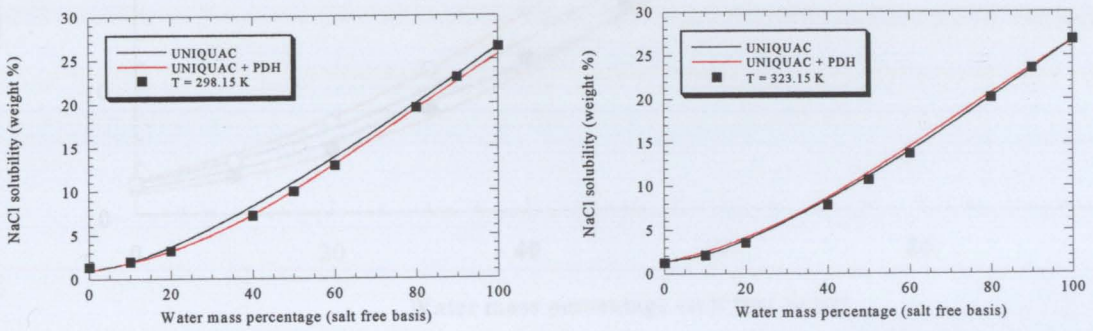

Figure 4.4 Experimental data and correlated curves for water/methanol/NaCl at 298.15 K and 323.15 K.

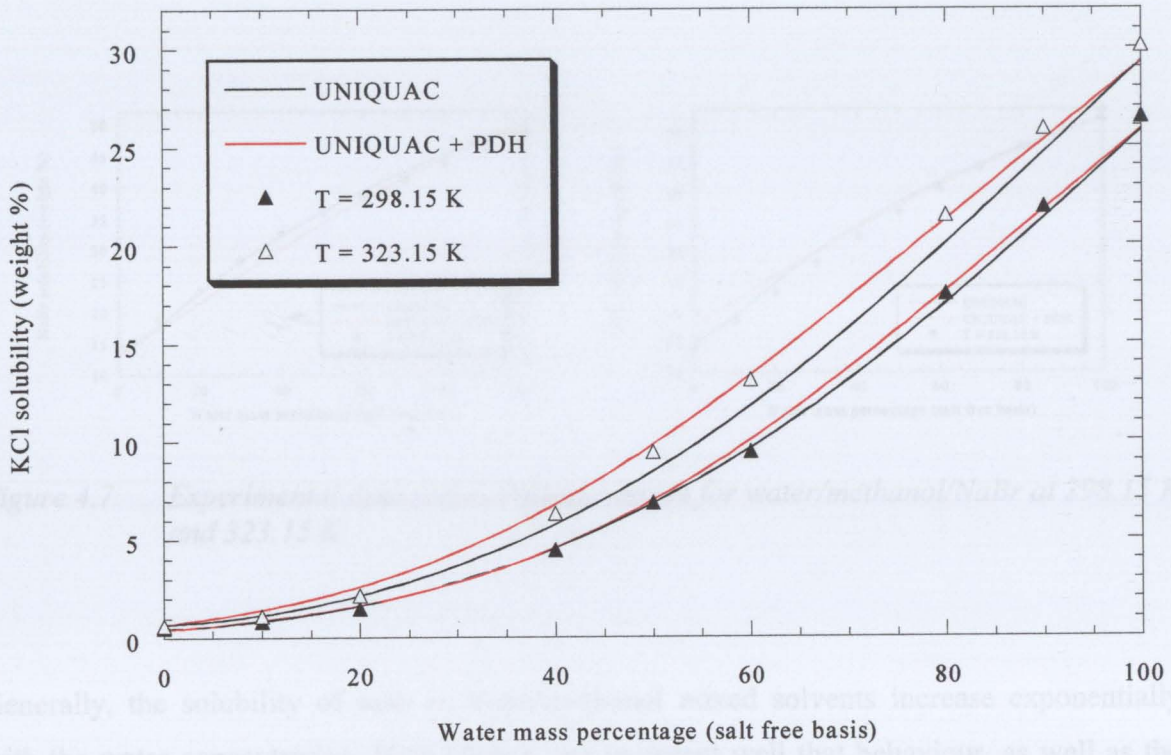

Figure 4.5 Experimental data and correlated curves for water/methanol/KCl.

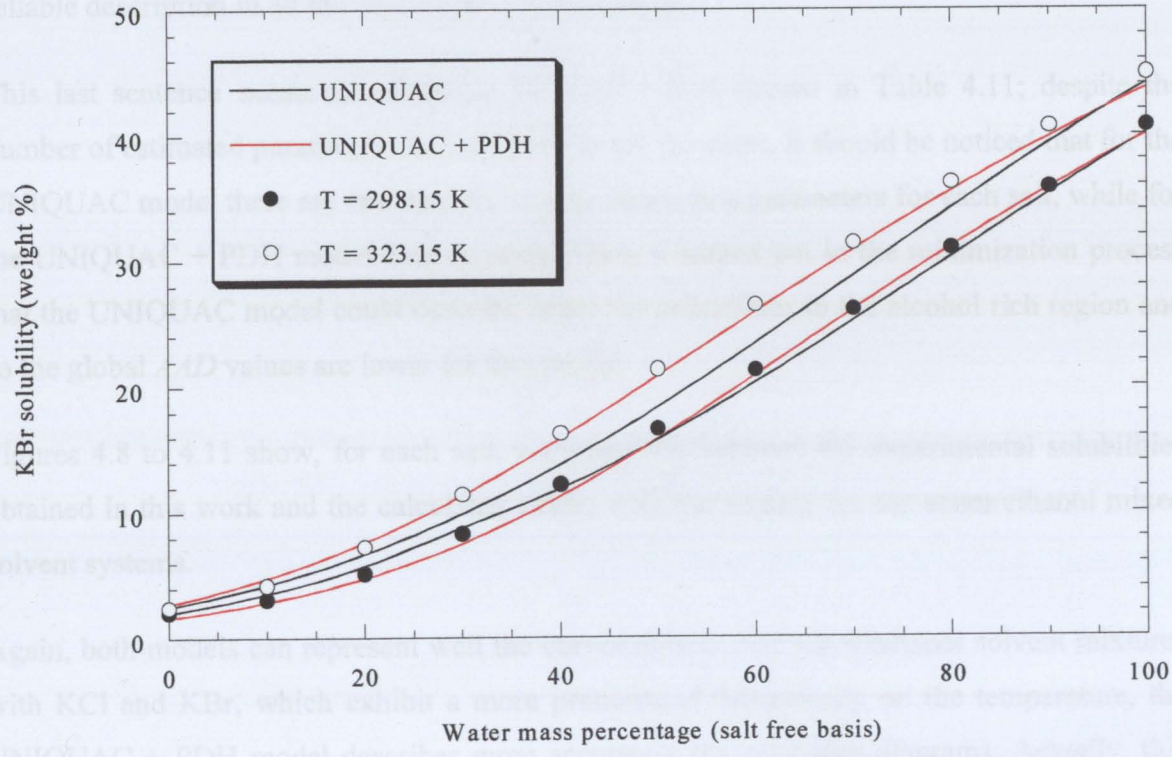

Figure 4.6 Experimental data and correlated curves for water/methanol/KBr.

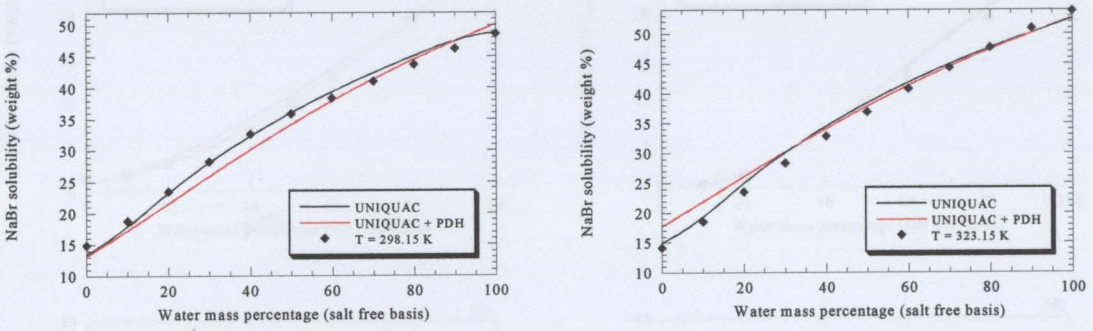

Figure 4.7 *Experimental data and correlated curves for water/methanol/NaBr at 298.15 K and 323.15 K.*

Generally, the solubility of salts in water/methanol mixed solvents increase exponentially with the water concentration. Both models can represent well that behaviour, as well as the curves shapes, convex for the NaBr solubility and concave for the other salts. However, excepting the water/ methanol/NaBr system, the UNIQUAC + PDH model presents a more reliable description in all the composition solvent range.

This last sentence seems to contradict the *AAD* values shown in Table 4.11; despite the number of estimated parameters for both models are the same, it should be noticed that for the UNIQUAC model there are two specific energy interaction parameters for each salt, while for the UNIQUAC + PDH model there is none. Thus, it turned out in the minimization process that the UNIQUAC model could describe better the solubilities in the alcohol rich region and so the global *AAD* values are lower for that model.

Figures 4.8 to 4.11 show, for each salt, a comparison between the experimental solubilities obtained in this work and the calculated values with the models for the water/ethanol mixed solvent systems.

Again, both models can represent well the curves shapes. For water/ethanol solvent mixtures with KCl and KBr, which exhibit a more pronounced dependency on the temperature, the UNIQUAC + PDH model describes more accurately the solubility diagrams. Actually, this model shows lower *AAD* for all the studied salts.

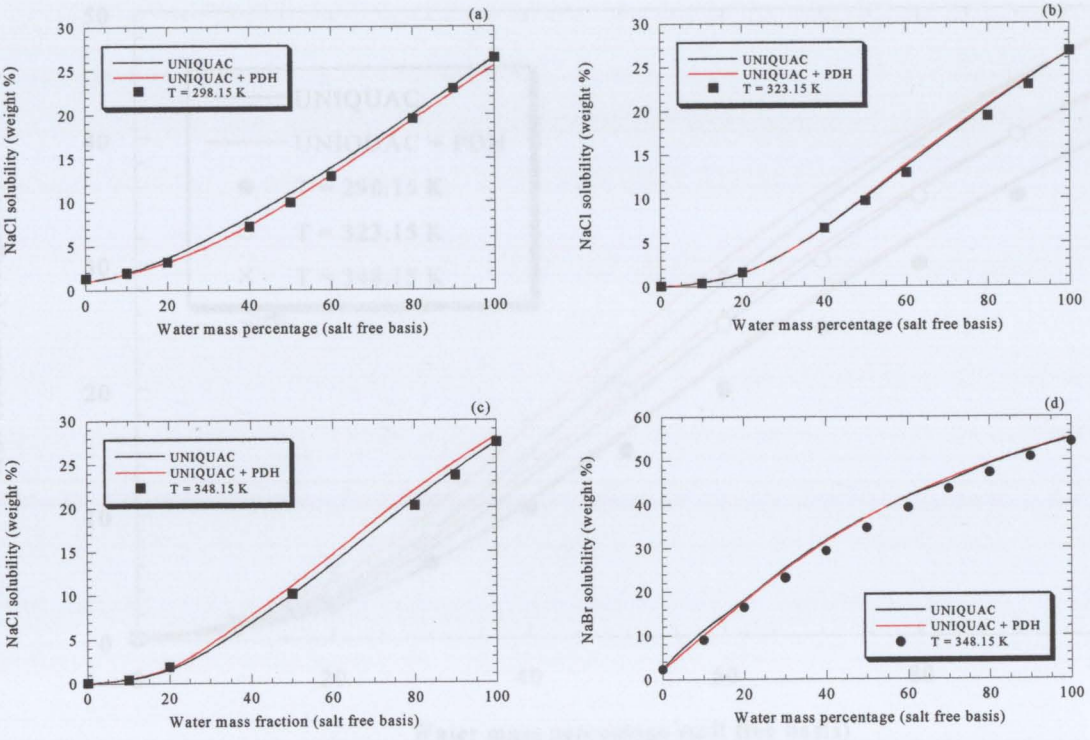

Figure 4.8 Experimental data and correlated curves for water/ethanol/salt: (a) NaCl (298.15 K) (b) NaCl (323.15 K) (c) NaCl (348.15 K) (d) NaBr (348.15 K).

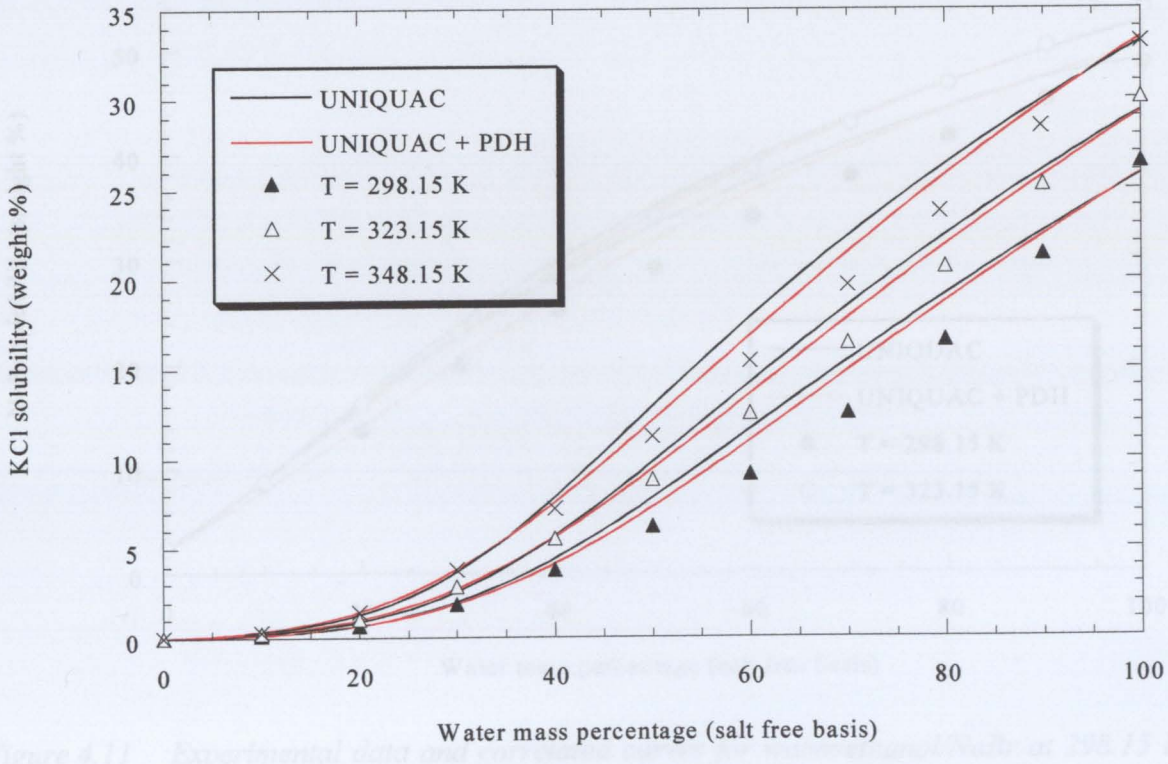

Figure 4.9 Experimental data and correlated curves for water/ethanol/KCl.

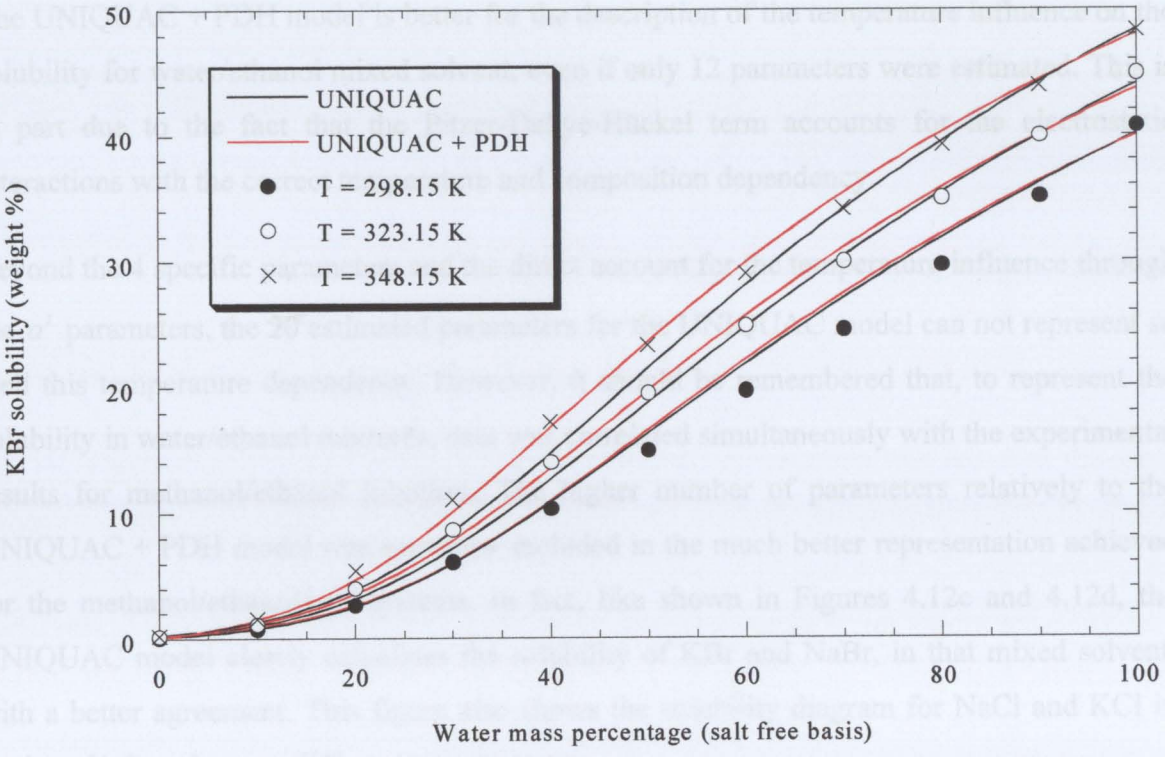

Figure 4.10 Experimental data and correlated curves for water/ethanol/KBr.

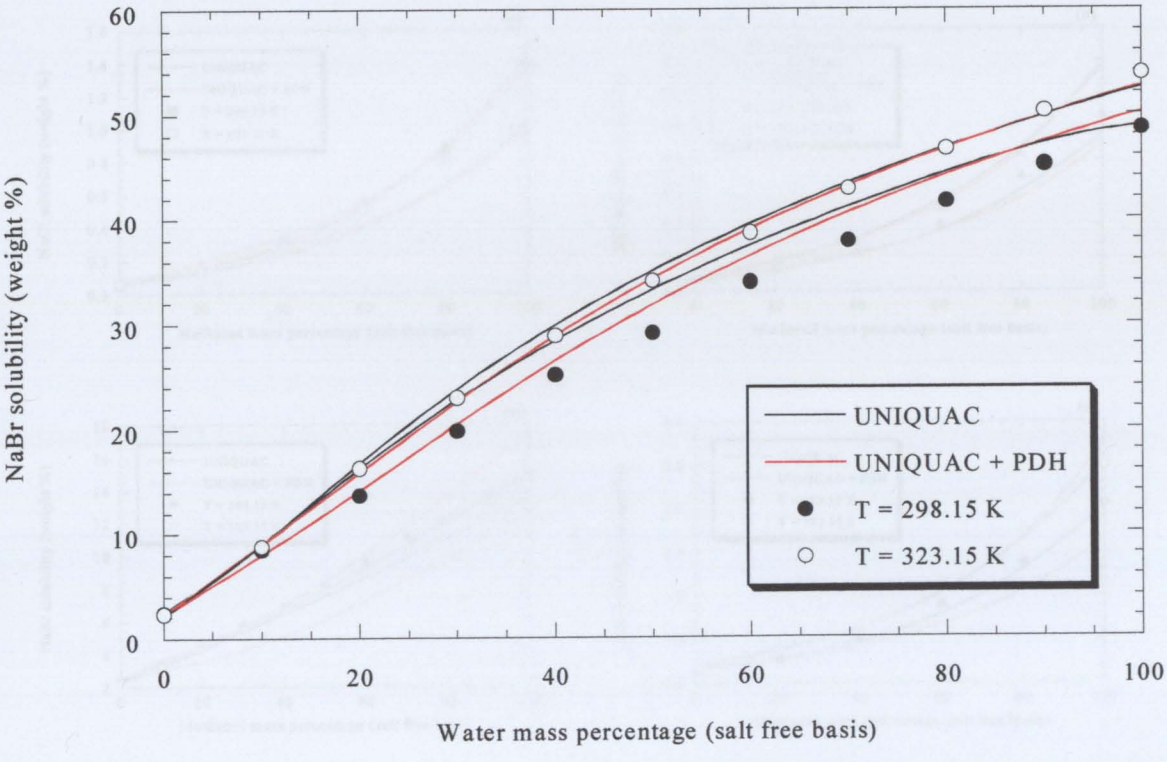

Figure 4.11 Experimental data and correlated curves for water/ethanol/NaBr at 298.15 K and 323.15 K.

The UNIQUAC + PDH model is better for the description of the temperature influence on the solubility for water/ethanol mixed solvent, even if only 12 parameters were estimated. This is in part due to the fact that the Pitzer-Debye-Hückel term accounts for the electrostatic interactions with the correct temperature and composition dependency.

Beyond the 4 specific parameters and the direct account for the temperature influence through the a^t parameters, the 20 estimated parameters for the UNIQUAC model can not represent so well this temperature dependency. However, it should be remembered that, to represent the solubility in water/ethanol mixtures, data was correlated simultaneously with the experimental results for methanol/ethanol mixtures. The higher number of parameters relatively to the UNIQUAC + PDH model was somehow included in the much better representation achieved for the methanol/ethanol/salt systems. In fact, like shown in Figures 4.12c and 4.12d, the UNIQUAC model clearly calculates the solubility of KBr and NaBr, in that mixed solvent, with a better agreement. This figure also shows the solubility diagram for NaCl and KCl in methanol/ethanol at two different temperatures.

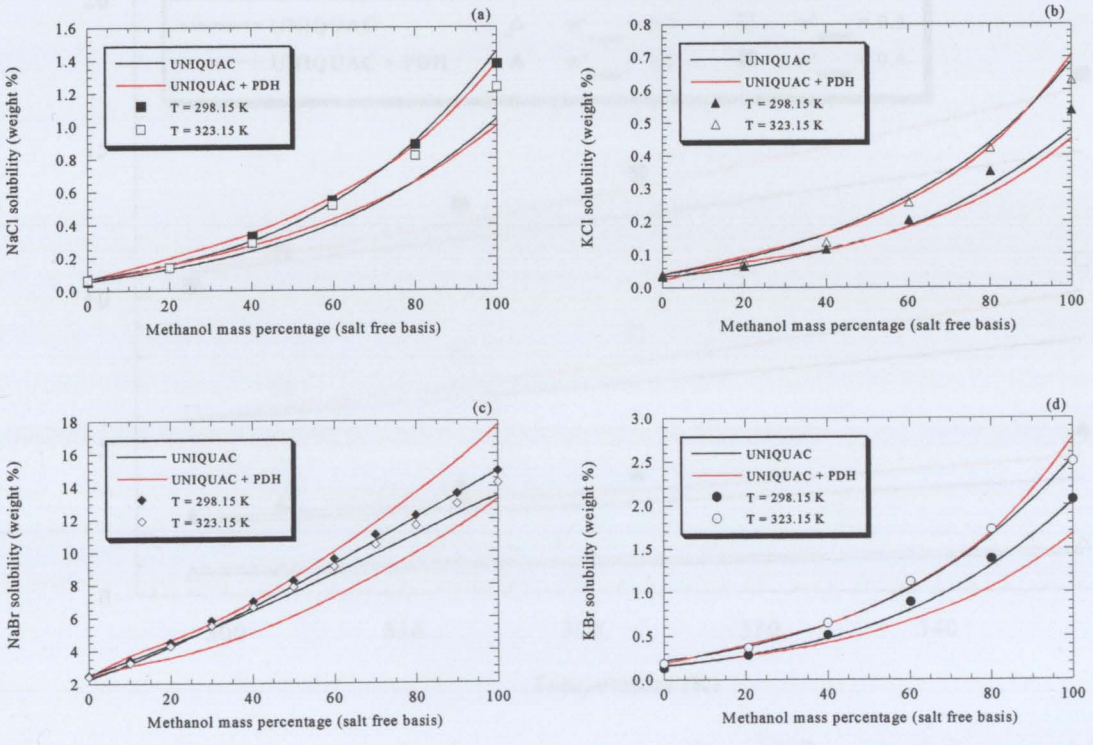

Figure 4.12 Experimental data and correlated curves for methanol/ethanol/salt: (a) NaCl (b) KCl (c) NaBr (d) KBr.

Despite the uncommon values obtained for the *AAD*, reported in Table 4.11, for methanol/ethanol/NaCl system, the graphical representation (Figure 4.12a) shows a good agreement between the correlated curves and the experimental points at 323.15 K, while at 298.15 K the results are poor. However, like has already been stated, in these systems the solubility is so low, that a small difference between the experimental solubility and the calculated one give rises to a very high absolute deviation.

For the water/ethanol/KBr system, reliable experimental information was found at the same solvent compositions of the present study, but at two different temperatures, 303.15 K and 313.15 K (Stephen and Stephen, 1964). Thus, in Figures 4.13 and 4.14 a comparison of the performance of both models in the description of the temperature effect on the solubility, at a fixed solvent composition, is given. The results are very satisfactory, being the UNIQUAC + PDH model the best for almost all the solvent compositions.

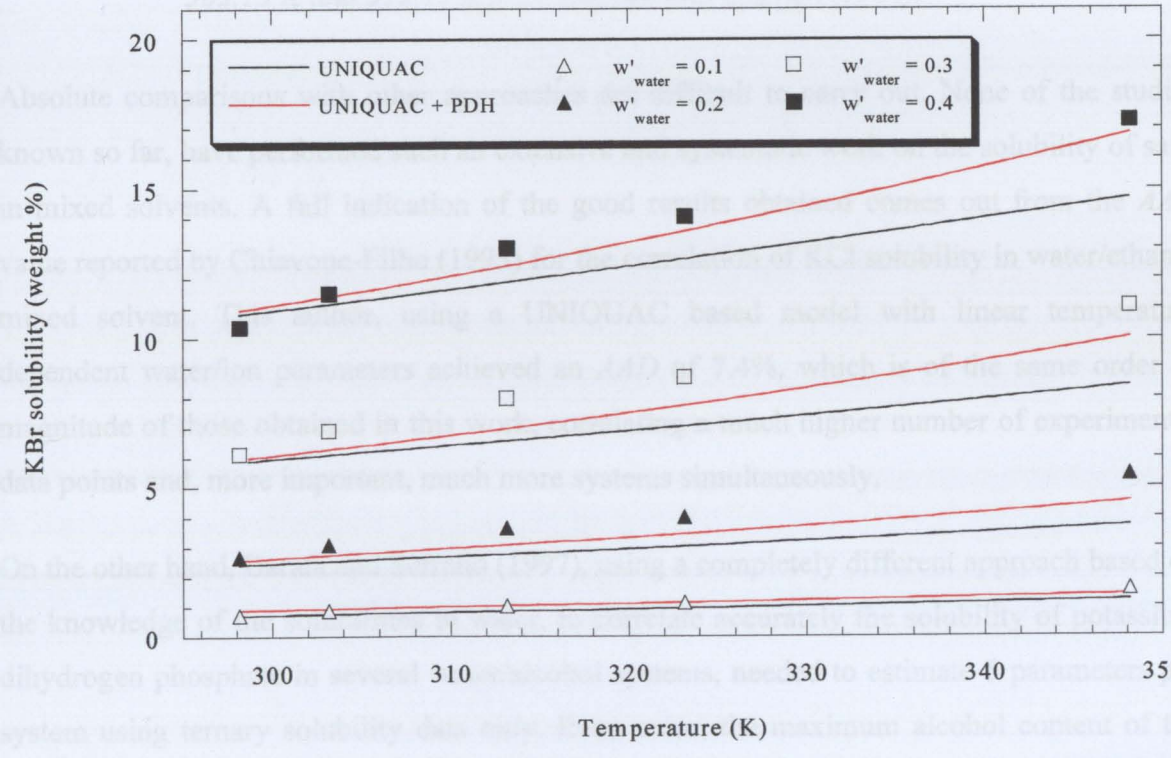

Figure 4.13 *Phetostatic curves for the system water/ethanol/KBr: correlation capabilities of the UNIQUAC and UNIQUAC + PDH models. Experimental results at 303.15 K and 313.15 K from Stephen and Stephen (1964).*

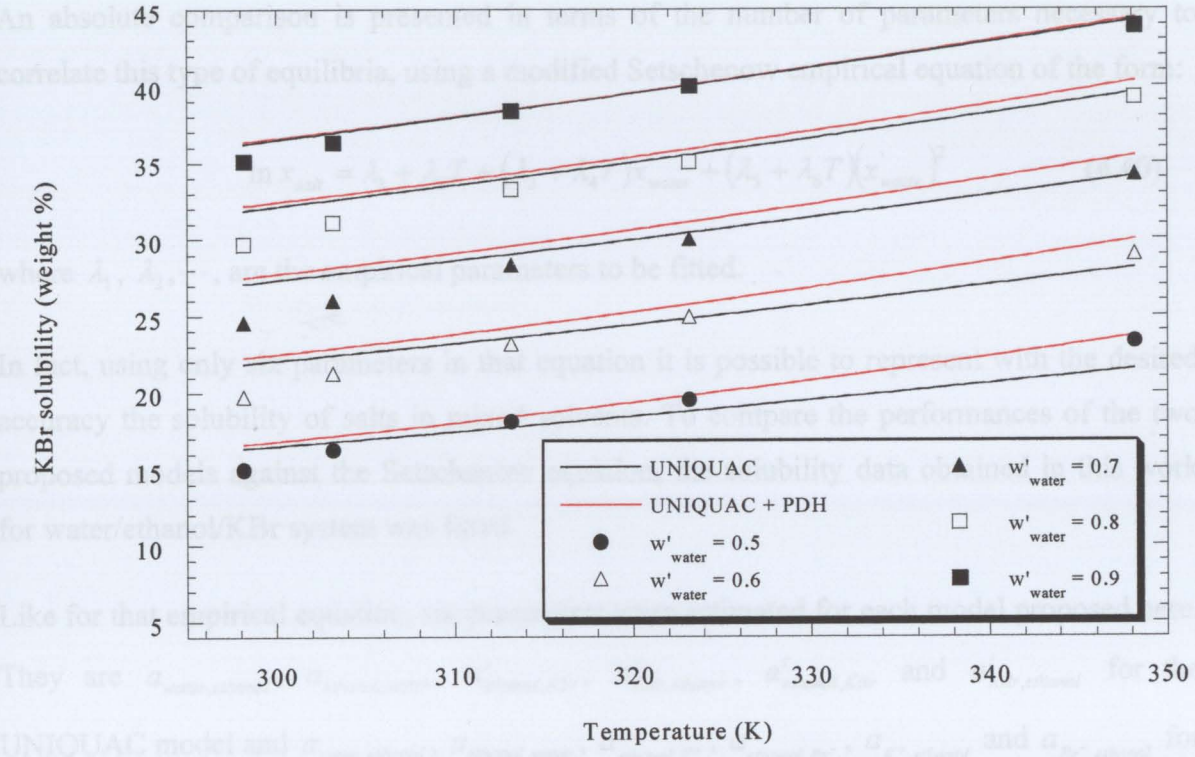

Figure 4.14 *Phetostatic curves for the system water/ethanol/KBr: correlation capabilities of the UNIQUAC and UNIQUAC + PDH models. Experimental results at 303.15 K and 313.15 K from Stephen and Stephen (1964).*

Absolute comparisons with other approaches are difficult to carry out. None of the studies known so far, have performed such an extensive and systematic work on the solubility of salts in mixed solvents. A full indication of the good results obtained comes out from the *AAD* value reported by Chiavone-Filho (1993) for the correlation of KCl solubility in water/ethanol mixed solvent. This author, using a UNIQUAC based model with linear temperature dependent water/ion parameters achieved an *AAD* of 7.4%, which is of the same order of magnitude of those obtained in this work, correlating a much higher number of experimental data points and, more important, much more systems simultaneously.

On the other hand, Barata and Serrano (1997), using a completely different approach based on the knowledge of the solubilities in water, to correlate accurately the solubility of potassium dihydrogen phosphate in several water/alcohol systems, needed to estimate 5 parameters per system using ternary solubility data only. Even more, the maximum alcohol content of the solvent mixture was 0.23 (alcohol mass fraction on salt free basis) and the temperature range 41.5 K. So, this confirms the extreme difficulty in the establishment of a rigorous model to correlate and predict salt solubility in mixed solvents. Therefore, the approach presented here is very useful and successful.

An absolute comparison is presented in terms of the number of parameters necessary to correlate this type of equilibria, using a modified Setschenow empirical equation of the form:

$$\ln x_{salt} = \lambda_1 + \lambda_2 T + (\lambda_3 + \lambda_4 T) x'_{water} + (\lambda_5 + \lambda_6 T)(x'_{water})^2 \qquad (4.40)$$

where λ_1, λ_2, $\cdots$, are the empirical parameters to be fitted.

In fact, using only six parameters in that equation it is possible to represent with the desired accuracy the solubility of salts in mixed solvents. To compare the performances of the two proposed models against the Setschenow equation, the solubility data obtained in this work for water/ethanol/KBr system was fitted.

Like for that empirical equation, six parameters were estimated for each model proposed here. They are $a_{water,ethanol}$, $a_{ethanol,water}$, $a^{\circ}_{ethanol,KBr}$, $a^{\circ}_{KBr,ethanol}$, $a^{t}_{ethanol,KBr}$ and $a^{t}_{KBr,ethanol}$ for the UNIQUAC model and $a_{water,ethanol}$, $a_{ethanol,water}$, $a_{ethanol,K^+}$, $a_{ethanol,Br^-}$, $a_{K^+,ethanol}$ and $a_{Br^-,ethanol}$ for the UNIQUAC + PDH model.

The results, in terms of *AAD*, with this methodology, for the UNIQUAC model, the UNIQUAC + PDH model, and the Setschenow equation are, respectively, 2.7, 3.5, and 4.1%. Indeed, the UNIQUAC model represents more accurately the salt solubility diagram for the water/ethanol/KBr system.

Figure 4.15 presents a comparison between the performances of the UNIQUAC model and the Setschenow equation in the calculation of the solubility of KBr in water/ethanol mixed solvent. In fact, the UNIQUAC model gives a more precise description of both the influence of the temperature and of the solvent composition on the KBr solubility.

A similar comparison is shown in Figure 4.16 between the capabilities of the UNIQUAC + PDH model and the Setschenow equation. The UNIQUAC + PDH model, like indicated by the *AAD* value is better, but the distinction is not so perceptible as in the previous case.

This study was also carried out for other systems, namely the water/ethanol/KCl system. The accuracy achieved with the equations studied follow the same trend as before. Thus, if the correlation of salt solubility is needed for a particular system, the UNIQUAC model and this new developed methodology should be applied.

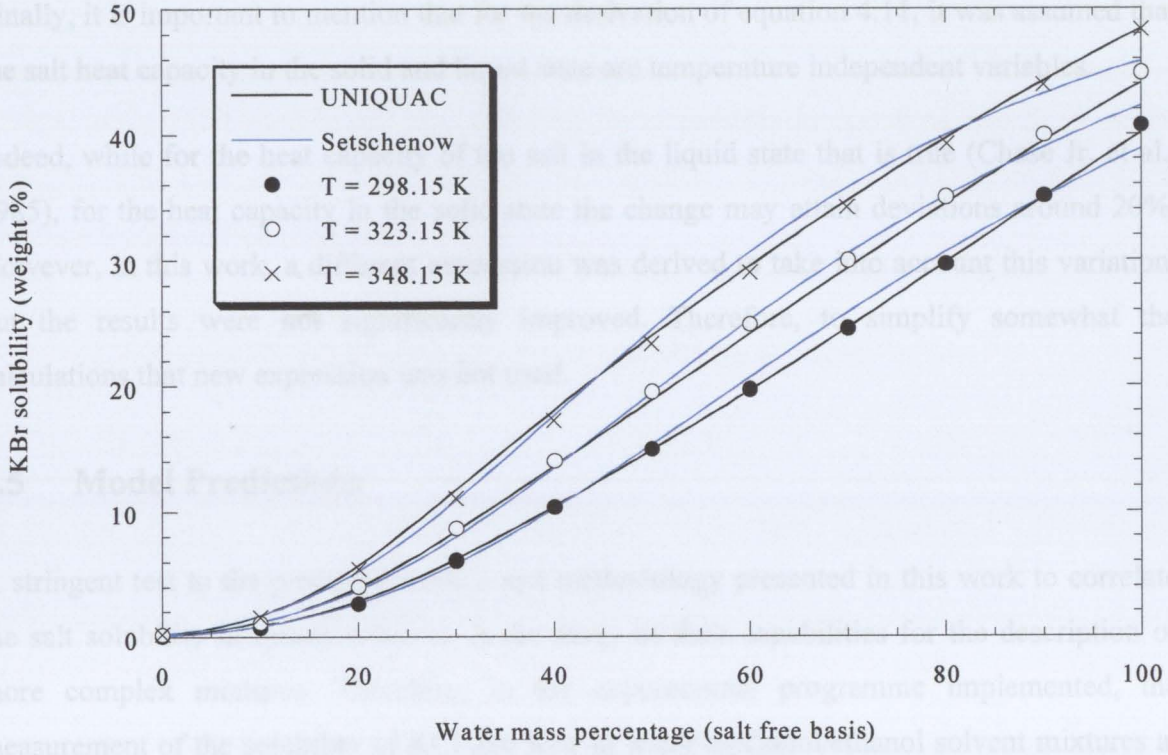

Figure 4.15 Solubility diagram for water/ethanol/KBr: comparison between the UNIQUAC model and the modified Setschenow equation.

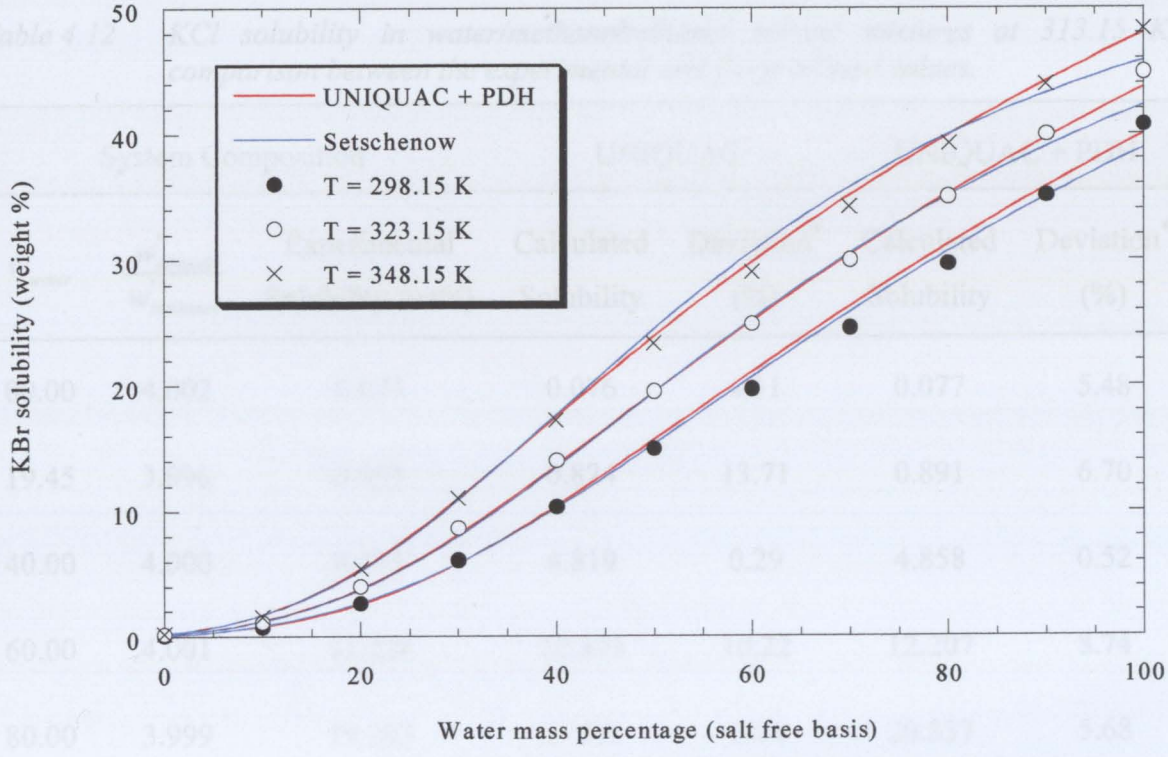

Figure 4.16 Solubility diagram for water/ethanol/KBr: comparison between the UNIQUAC + PDH model and the modified Setschenow equation.

Finally, it is important to mention that for the derivation of equation 4.11, it was assumed that the salt heat capacity in the solid and liquid state are temperature independent variables.

Indeed, while for the heat capacity of the salt in the liquid state that is true (Chase Jr. et al., 1985), for the heat capacity in the solid state the change may attain deviations around 20%. However, in this work, a different expression was derived to take into account this variation, but the results were not significantly improved. Therefore, to simplify somewhat the calculations that new expression was not used.

4.5 Model Predictions

A stringent test to the proposed models and methodology presented in this work to correlate the salt solubility in mixed solvents, is the study of their capabilities for the description of more complex mixtures. Therefore, in the experimental programme implemented, the measurement of the solubility of KCl and KBr in water/methanol/ethanol solvent mixtures at 313.15 K was carried out. It should be noticed that this temperature value was not considered for the measurements for the ternary systems.

Table 4.12 KCl solubility in water/methanol/ethanol solvent mixtures at 313.15 K: comparison between the experimental and the predicted values.

System Composition			UNIQUAC		UNIQUAC + PDH	
w'_{water}	$\frac{w'_{ethanol}}{w'_{methanol}}$	Experimental Solubility (*wt%*)	Calculated Solubility	Deviation* (%)	Calculated Solubility	Deviation* (%)
00.00	4.002	0.073	0.076	4.11	0.077	5.48
19.45	3.996	0.955	0.824	13.71	0.891	6.70
40.00	4.000	4.833	4.819	0.29	4.858	0.52
60.00	4.001	11.226	12.373	10.22	12.207	8.74
80.00	3.999	19.282	20.543	6.54	20.337	5.68
	Average			6.97		5.42

*deviation (%) = $\left|(experimental - calculated)/experimental\right| * 100$

Tables 4.12 and 4.13 summarize the results obtained for the predictions. The deviations between the experimental solubilities and the calculated values with the UNIQUAC and the UNIQUAC + PDH models are also indicated. It is possible to conclude that the average deviation, with both models, is around 7% and, therefore, the models can be used with good accuracy for prediction purposes.

Table 4.13 KBr solubility in water/methanol/ethanol solvent mixtures at 313.15 K: comparison between the experimental and the predicted values.

System Composition			UNIQUAC		UNIQUAC + PDH	
w'_{water}	$\frac{w'_{ethanol}}{w'_{methanol}}$	Experimental Solubility (*wt%*)	Calculated Solubility	Deviation* (%)	Calculated Solubility	Deviation* (%)
00.00	1.000	0.790	0.730	7.59	0.672	14.94
20.00	1.001	4.553	3.976	12.67	3.687	19.02
40.00	1.001	13.277	11.831	10.89	12.103	8.84
59.93	1.000	23.492	22.487	4.28	23.538	0.20
79.98	1.001	33.631	33.218	1.23	33.925	0.87
	Average			7.33		8.77

*deviation (%) = $\left|(experimental - calculated)/experimental\right| * 100$

The good quality of the predictions can be seen in Figures 4.17 and 4.18. In fact, while for the solubility of KCl in water/methanol/ethanol mixed solvent the predicted curves are quite similar, the same does not happen for the KBr solubility. For the representation of the salt solubility diagram in this last case, the UNIQUAC + PDH model gives a better agreement in all the solvent composition range. Actually, the average deviations given in Table 4.13 are not the best measures to compare the predicting capabilities of the models since much higher deviations are observed for the UNIQUAC + PDH model in the high alcohol content region of the mixed solvent. Since the solubilities are much lower in that zone, a small difference between the experimental and calculated solubility values gives rise to high deviations.

The results for the predictions are extremely encouraging. However, it would be nice to have more experimental determinations to confirm the obtained results.

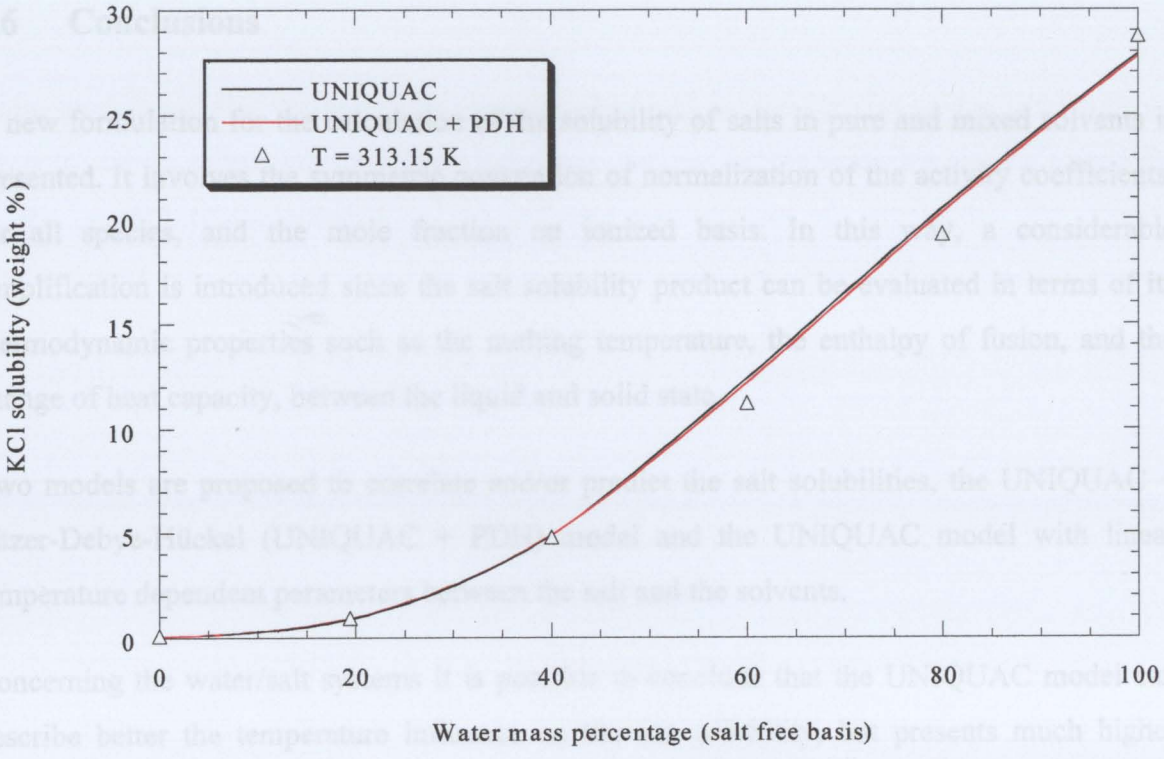

Figure 4.17 Experimental data and predicted curves for the solubility of KCl in the water(1)/ methanol(2)/ ethanol(3) mixed solvent ($w_3'/w_2' = 4.00$).

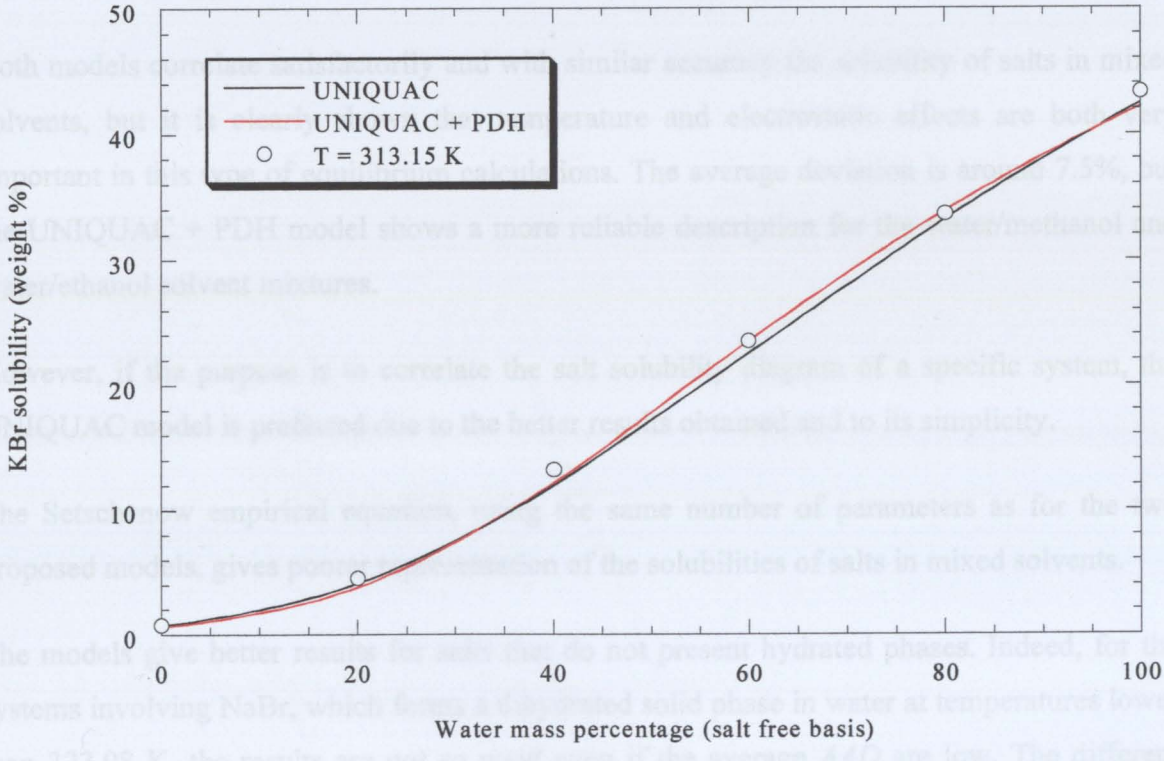

Figure 4.18 Experimental data and predicted curves for the solubility of KBr in the water(1)/ methanol(2)/ ethanol(3) mixed solvent ($w_3'/w_2' = 1.00$).

4.6 Conclusions

A new formulation for the calculation of the solubility of salts in pure and mixed solvents is presented. It involves the symmetric convention of normalization of the activity coefficients, for all species, and the mole fraction on ionized basis. In this way, a considerable simplification is introduced since the salt solubility product can be evaluated in terms of its thermodynamic properties such as the melting temperature, the enthalpy of fusion, and the change of heat capacity, between the liquid and solid state.

Two models are proposed to correlate and/or predict the salt solubilities, the UNIQUAC + Pitzer-Debye-Hückel (UNIQUAC + PDH) model and the UNIQUAC model with linear temperature dependent parameters between the salt and the solvents.

Concerning the water/salt systems it is possible to conclude that the UNIQUAC model can describe better the temperature influence on the salt solubility, but presents much higher deviations than the UNIQUAC + PDH model in the representation of osmotic coefficients. This confirms the need of a Debye-Hückel expression type to account for the electrostatic forces in electrolyte systems, at least for the dilute salt region.

Both models correlate satisfactorily and with similar accuracy the solubility of salts in mixed solvents, but it is clearly shown that temperature and electrostatic effects are both very important in this type of equilibrium calculations. The average deviation is around 7.5%, but the UNIQUAC + PDH model shows a more reliable description for the water/methanol and water/ethanol solvent mixtures.

However, if the purpose is to correlate the salt solubility diagram of a specific system, the UNIQUAC model is preferred due to the better results obtained and to its simplicity.

The Setschenow empirical equation, using the same number of parameters as for the two proposed models, gives poorer representation of the solubilities of salts in mixed solvents.

The models give better results for salts that do not present hydrated phases. Indeed, for the systems involving NaBr, which forms a dihydrated solid phase in water at temperatures lower than 323.98 K, the results are not so good even if the average *AAD* are low. The different solubility trends in systems involving the salt NaBr are difficult to describe, suggesting a study of the different solid phases that may appear.

These models and this methodology are a valuable tool for the correlation and prediction of salt solubility in mixed solvents. The predictions obtained for the solubilities of KCl and KBr in the water/methanol/ethanol mixed solvent are motive of stimulation for further developments.

List of Symbols

a	activity
a	UNIQUAC interaction parameter, K
$A_{DH,x}$	constant defined according to equation 4.24
b	parameter in Pitzer-Debye-Hückel equation
C_p	heat capacity
e	electronic charge, C
f	rational activity coefficient
G	Gibbs energy
H	enthalpy
I	ionic strength
k	Boltzmann constant, JK^{-1}
K	solubility product
l	parameter in equation 4.17
l	liquid state
m	molality
M	cation
n	mole number
N_A	Avogrado's number, mol^{-1}
N_{data}	number of experimental data points
N_{ion}	total number of ions
N_{spec}	total number of species
N_{SLE}	number of experimental solubility results
N_{solv}	total number of solvents
N_{VLE}	number of experimental osmotic coefficients results
q	surface area parameter of a species
Q	coefficient in equation 4.8
r	van der Waals volume parameter of a species
R	ideal gas constant, $calmol^{-1}K^{-1}$
s	solid state
T	absolute temperature, K
w	mass percentage

$wt\%$	mass percentage
x	mole fraction in the liquid phase
$\underline{x}$	mole fraction composition vector
X	anion
y	salt solubility or osmotic coefficient
z	ionic charge

Greek Letters

Δ	property difference
ε	solvent dielectric constant
$\varepsilon_\circ$	vacuum permittivity, $C^2J^{-1}m^{-1}$
θ	area fraction of a species
λ	parameter according to equation 4.40
μ	chemical potential
ν	stoichiometric coefficient of the ion
ρ	density, $kmoldm^{-3}$
$\rho_\circ$	solvent density, $molcm^{-3}$
τ	parameter according to equation 4.21
ϕ	volume fraction of a species or osmotic coefficient
φ	volumetric fraction in salt free basis
ω	weighting factor

Subscripts

d	data set number d
f	property at fusion point
i	any species
j	any species
k	any species
l	ion species or salt
m	solvent species
ms	mixed solvent
p	experimental data point
PDH	Pitzer-Debye-Hückel model

salt	salt
std	standard
UNIQUAC	UNIQUAC model
x	property on mole fraction basis
+	cation
−	anion
±	mean ionic property

Superscripts

calc	calculated by the model
C	combinatorial
exp	experimental
E	excess property
PDH	Pitzer-Debye-Hückel model
R	residual
t	dependent temperature parameter
UNIQUAC	UNIQUAC model
°	standard state
•	pure solvent property
∇	pure salt property
'	salt free basis

Abbreviations

AAD	average absolute deviation
OBJ	objective function
PDH	Pitzer-Debye-Hückel
SLE	solid-liquid equilibrium
VLE	vapour-liquid equilibrium

Chapter 5

SOLID-LIQUID EQUILIBRIUM IN WEAK ELECTROLYTE SYSTEMS

5. Solid-Liquid Equilibrium in Weak Electrolyte Systems

5.1 Introduction

The knowledge of fundamental physical properties like the activity coefficients and solubilities of biomolecules in water is extremely important for the biochemical industry. Amino acids and peptides are among those substances and in solution they behave like weak electrolytes. Thus, in this work a new model is proposed to represent the activity coefficients of amino acids and small peptides in water. The UNIFAC model is combined with a Debye-Hückel term to describe the activity coefficients of the species present in the biomolecule/water systems. New groups are defined according to the group-contribution concept, and chemical equilibrium is taken into account simultaneously with the physical equilibrium. To estimate the new interaction parameters, molal activity coefficient data from the literature are used. These parameters, in addition to solubility data, are the basis for the correlation of the solubility product of the amino acids. Using this approach, very satisfactory results can be obtained for the representation and prediction of the solubilities of amino acids in aqueous solutions at different conditions of temperature and pH.

5.1.1 Importance of the Subject

Many valuable biochemicals are produced in reactors where the product concentration in a very complex mixture is very small. Therefore, the development of efficient methods for separation, concentration, and purification of biological products is of fundamental importance.

To design, optimize, and scale-up separation processes, the application of molecular thermodynamics is a very useful tool. In the case of biotechnology, it is particularly important to focus the attention on the properties of aqueous systems containing salts and large, charged molecules (Prausnitz, 1989). Although amino acids are among the simplest biochemical molecules, they have many similarities with more complex biomolecules such as antibiotics (Orella and Kirwan, 1991) and are the building blocks of all proteins. Therefore, the study of their solubility in water is a good starting point for the understanding of biochemical systems.

5.1.2 Previous Modelling Work

The successful representation of the solubilities is directly related to the ability of correlating and predicting the activity coefficients of the amino acids in the aqueous solution. In this way, several attempts have been made in the recent past:

Nass (1988) has assumed the activity coefficients of amino acids to be a product of two terms due to chemical reaction equilibria and physical interactions. For this last term the author uses the Wilson equation (Wilson, 1964), with Bondi's volume ratios (Bondi, 1968) as pure-component liquid volume ratios. As the data were correlated for each amino acid separately, the corresponding results are satisfactory. However, the study is limited to a few amino acids and the number of estimated parameters attain, like for the representation of the solubility of diiodotyrosine in water, values as high as 10.

Chen et al. (1989) added two different contributions for the calculation of the excess Gibbs energy of the system: one is the result of the long-range interactions and was represented by a Pitzer-Debye-Hückel term (Pitzer, 1980); the other is due to local interaction and was formulated through a modified form of the NRTL equation (Renon and Prausnitz, 1968) with two adjustable parameters for each amino acid/water pair. The correlations were also done individually for each amino acid, and the results are very satisfactory, both for the correlation of the activity coefficients and solubilities.

One year later, Gupta and Heidemann (1990) tried to describe the activity coefficients of amino acids in water considering only short-range interactions, using the modified UNIFAC model (Larsen et al., 1987). Their definition of groups is different from the usual, as they considered very large groups. The proline molecule, for instance, was considered one single group. In average, the results may be considered poor both for correlation and prediction.

Peres and Macedo (1994) carried out a fundamental study with the modified UNIQUAC model for electrolytes originally proposed by Sander et al. (1986) and later revised by Macedo et al. (1990). Once more, the correlation was done each amino acid at a time, achieving very good results.

In a more recent work, Kuramochi et al. (1996) based on the UNIFAC model by Larsen et al. (1987), divided the CH_2 group in two new groups; $\alpha - CH$ and $sc - CH_2$ (side chain CH_2). In spite of the very high number of interaction parameters that arises from this change, the authors support it on the ability of this new model for the representation of the activity coefficients of amino acids with large hydrocarbon chain.

5.2 Model Development

In order to describe the solid-liquid equilibrium for the amino acid or peptide/water systems, the model proposed here takes into account the physical equilibrium simultaneously with the chemical equilibrium. In fact, as shown in the following sections, amino acids and peptides are weak electrolytes since they participate in a series of chemical reactions that give rise to different ionic species.

5.2.1 Phase and Chemical Equilibria

When an amino acid or a peptide (AA) is present in an aqueous solution (aq), some reactions take place. The solubleness of the solid (s) amino acid or peptide can be represented by:

$$AA(s) \xleftrightarrow{k_s} AA(aq) \tag{5.1}$$

with an equilibrium constant k_s.

Amino acids and peptides have, among others, an amino group and a carboxyl group, which are ionized in aqueous solutions, giving rise to a neutral dipolar species called a zwitterion ($AA^{\pm}$), carrying dual electric charges, a positive one in the amino group and a negative in the carboxyl group. This is written in the next equation:

$$AA(aq) \xleftrightarrow{K_D} AA^{\pm}(aq) \tag{5.2}$$

The participation of the zwitterion in acid-base reactions to form biomolecule anionic (AA^-) or cationic (AA^+) species is shown by equations 5.3 and 5.4, respectively:

$$AA^+ \xleftrightarrow{K_1} AA^{\pm} + H^+ \tag{5.3}$$

$$AA^{\pm} \xleftrightarrow{K_2} AA^- + H^+ \tag{5.4}$$

The chemical equilibrium constants for equations 5.2 to 5.4 are respectively K_D, K_1 and K_2. It is worthwhile to mention that some amino acids have more than one cationic species, such as arginine and lysine, or more than one anionic species, like tyrosine and aspartic acid (Bohinski, 1987). However, in this study only molecules with two acid-base reactions were considered. Peres and Macedo (1994) adopted this same assumption.

Finally, the water decomposition into the hydrogen (H^+) and the hydroxyl (OH^-) ions should also be taken into account using the ionic product of water (K_w) as shown by equation 5.5:

$$H_2O \xleftrightarrow{K_w} H^+ + OH^- \tag{5.5}$$

Greenstein and Winitz (1961) reported values of K_D for amino acids and small peptides in the range $10^5 - 10^6$. Thus, equations 5.1 and 5.2 can be combined as follows:

$$AA(s) \xleftrightarrow{K_S} AA^{\pm}(aq) \tag{5.6}$$

Equation 5.6 indicates the dissolution of a biomolecule, forming the zwitterion.

As can be seen in Figure 5.1, in isoelectric solutions, for which the isoelectric point is defined by $pI = pH = (pK_1 + pK_2)/2$, neutral dipolar species are predominant, but for pH much higher than pI, the anionic amino acid or peptide species become predominant, while cationic species are dominant at values of pH much smaller than pI.

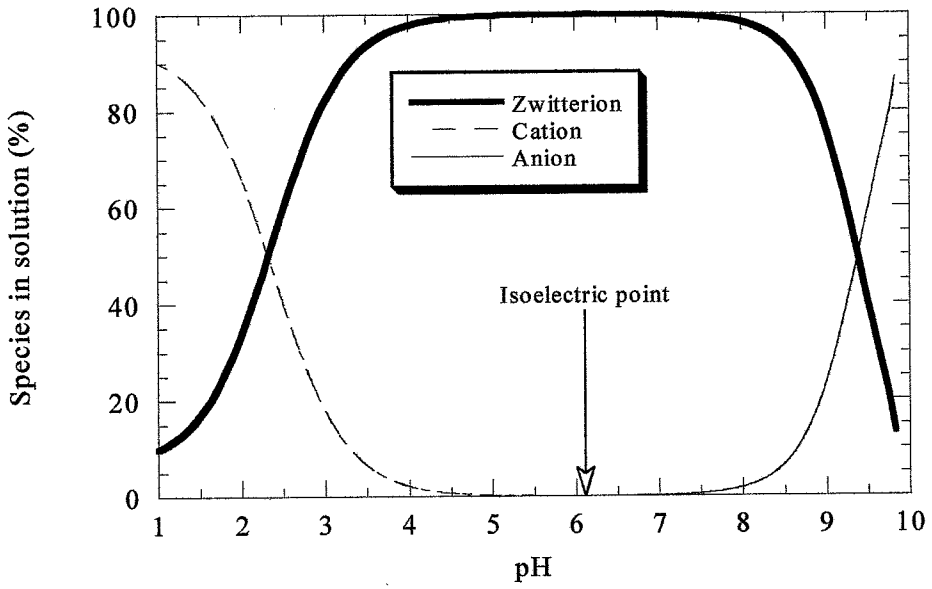

Figure 5.1 *Percentage of the different glycine ionic species in aqueous solution at 298.15 K as a function of pH.*

Therefore, to accurately describe the behaviour of aqueous biomolecule solutions in terms of its composition it is necessary to use the equilibrium constants. Assuming pure solid phase:

$$K_s = a^m_{AA^{\pm}} \tag{5.7}$$

The other equilibrium constants are given by:

$$K_1 = a^m_{AA^{\pm}} a^m_{H^+} / a^m_{AA^+} \tag{5.8}$$

$$K_2 = a^m_{AA^-} a^m_{H^+} / a^m_{AA^{\pm}} \tag{5.9}$$

$$K_w = a^m_{H^+} a^m_{OH^-} \tag{5.10}$$

where for any species,

$$a^m_i = m_i \gamma^*_i \tag{5.11}$$

In these equations, a^m_i is the activity of species i in the molality scale, γ^* is the unsymmetric molal activity coefficient, and m the molality. So, it becomes evident that for the successful representation of the solubilities and their dependency with pH and temperature it is necessary to be able to correctly represent the activity coefficients of the different species in

the solution. However, this is not an easy task. Besides the powerful electric fields surrounding the charged groups that give rise to important long-range interactions and in a certain way make amino acids and peptides behave as strong electrolytes (Cohn et al., 1934), the influence of the hydrocarbon chain must also be taken into consideration.

5.2.2 Proposed Model for the Activity Coefficients

To represent these physical interactions, a semi-empirical model is proposed. The model is based on the assumption that the unsymmetric molar excess Gibbs function ($G^{*,E}$) of the system, on mole fraction basis, is a linear combination of two terms:

$$G^{*,E} = G^{*,E}_{UNIFAC} + G^{*,E}_{DH} \tag{5.12}$$

The UNIFAC group-contribution method (Fredenslund et al., 1975) has been widely used to describe the non-ideality in non-electrolyte systems (Gmehling et al., 1982; Macedo et al., 1983; Larsen et al., 1987; Tiegs et al., 1987; Hansen et al., 1991), as well as for phase equilibria in polymer solutions (Kontogeorgis et al., 1993; Zhong et al., 1996; Pappa et al., 1997), but the extension to electrolyte or biochemical systems has been scarcely reported. The works by Gupta and Heidemann (1990), and Kuramochi et al. (1996) are the two unique attempts known to apply the UNIFAC equation to amino acid/water systems, not considering however, the long-range interaction forces represented in this work by the Debye-Hückel expression.

From equation 5.12 the rational unsymmetric activity coefficient for the ionic species can be derived as:

$$\ln f_i^* = \ln f_i^{*,UNIFAC} + \ln f_i^{*,DH} \tag{5.13}$$

The original UNIFAC model (Fredenslund et al., 1975) calculates the activity coefficient of species i (f_i^{UNIFAC}) in the mole fraction scale and symmetric convention according to:

$$\ln f_i^{UNIFAC} = \ln f_i^C + \ln f_i^R \tag{5.14}$$

The combinatorial term f_i^C used here, representing the differences in size and shape of the species in the system, is the one from the original equation with the correction introduced by Kikic et al. (1980) for very dilute solutions:

$$\ln f_i^C = \ln\frac{\Phi_i^c}{x_i} + 1 - \frac{\Phi_i^c}{x_i} - 5q_i\left(\ln\frac{\Phi_i}{\Theta_i} + 1 - \frac{\Phi_i}{\Theta_i}\right) \tag{5.15}$$

where,

$$\Phi_i^c = \frac{r_i^{2/3}x_i}{\sum_j r_j^{2/3}x_j} \tag{5.16}$$

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \tag{5.17}$$

$$\Theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{5.18}$$

In these equations x_i is the mole fraction of component i, j refers to all the number of molecules in the solution, and pure component parameters r_i and q_i are, respectively, measures of molecular van der Waals volumes and molecular surface areas, calculated as the sum of the group volume and group area parameters, R_k and Q_k;

$$r_i = \sum_k \nu_k^{(i)} R_k \tag{5.19}$$

$$q_i = \sum_k \nu_k^{(i)} Q_k \tag{5.20}$$

where k is the number of different functional groups in molecule i, and $\nu_k^{(i)}$ is the number of groups of type k present in the molecule.

The residual term, f_i^R, takes the short-range molecular energetic interactions into account, and is expressed as:

$$\ln f_i^R = \sum_k \nu_k^{(i)}\left(\ln\Gamma_k - \ln\Gamma_k^{(i)}\right) \tag{5.21}$$

Γ_k is the activity coefficient of group k in the solution, and $\Gamma_k^{(i)}$ is the activity coefficient of group k in a reference solution containing only molecules of type i.

The activity coefficient of group k is given by:

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \theta_m \tau_{mk} \right) - \sum_m \frac{\theta_m \tau_{km}}{\sum_n \theta_n \tau_{nm}} \right] \tag{5.22}$$

In these summations m and n concern to all the groups in the solution. The area fraction of group m (θ_m) is obtained using the following equations:

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{5.23}$$

$$X_m = \frac{\sum_j \nu_m^{(i)} x_j}{\sum_j \sum_n \nu_n^{(i)} x_j} \tag{5.24}$$

X_m is the fraction parameter of group m, j is the number of molecules in the mixture, and $\nu_m^{(i)}$ is the number of groups of type m in the molecule i.

The parameter τ is given by:

$$\tau_{nm} = \exp\left(-\frac{a_{nm}}{T} \right) \tag{5.25}$$

where a_{nm} is the UNIFAC interaction parameter between the groups n and m, and T is the absolute temperature of the mixture. Equations 5.22 to 5.25 are also used for the calculation of the activity coefficient of group k in the reference solution.

The conversion from the rational symmetric (f_i^{UNIFAC}) to the rational unsymmetric ($f_i^{*,UNIFAC}$) activity coefficients, is made using equation 2.19. Therefore, the calculation of the activity coefficients at infinite dilution, by means of the UNIFAC equations, must also be done.

The Debye-Hückel contribution presented in equation 5.13 is used to represent the long-range interaction forces. This term, expressed in chapter 2 by equations 2.46 to 2.49, computes solution ionic strength (I) from the net charge of the species, and therefore, for zwitterion this term is zero.

Finally, the conversion between rational activity coefficients calculated with equation 5.13, an the molal ones, is carried out using equation 5.26 from Table 2.2:

$$\gamma_i^* = x_w f_i^* \tag{5.26}$$

where x_w is the water mole fraction in the solution.

The use of this model requires:

- The knowledge of the dissociation equilibrium constants K_1, K_2, K_w, and their variation with the temperature, as well as the thermodynamic solubility constant K_s from equation 5.6.
- The temperature dependency of the Debye-Hückel parameters A and B, and the distance of closest approach a.
- The decomposition of the molecules of each component in their functional groups using those already available in the literature or defining new ones, their structural parameters R_k and Q_k, and finally the interaction parameters between the different groups present in the solution.

5.2.2.1 Equilibrium Constants and Debye-Hückel Parameters

The temperature dependency of the dissociation equilibrium constants K_1 and K_2, have been reported by several authors. The data used in this work were found in the CRC Handbook of Chemistry and Physics (Izatt and Christensen, 1973) and in King (1951). K_w values were taken from the book by Robinson and Stokes (1970), and the equilibrium constant K_s is regressed from solubility data as discussed later in section 5.3.

The parameters A and B in the Debye-Hückel equation were calculated according to equations 2.48 and 2.49, while the distance of closest approach a is taken as a constant equal to $4*10^{-8}m$.

The expressions used for the calculation of K_1, K_2, K_w, A and B are given in Appendix C.

5.2.2.2 Definition of New UNIFAC Groups

The philosophy beyond the group-contribution concept is to define small groups from which it is possible to build a considerable number of molecules. In the formulation of new groups a similar strategy as previously adopted for groups already available on the UNIFAC parameter tables was used, and whenever possible, those were used.

In the amino acid or peptide/water systems there are six species in solution ($AA^{\pm}$, AA^{-}, AA^{+}, H_2O, H^{+} and OH^{-}) which lead to an extremely high number of interaction parameters if all groups needed to describe all the present species are considered. Due to the high number of interaction parameters to be estimated and the relatively small amount of experimental data available some assumptions had to be made.

As discussed earlier (Figure 5.1) the zwitterionic species are predominant in pure water. It is then assumed that species H^{+} and OH^{-} do not have any contribution for the short-range forces since their concentration is very small at the isoelectric point. It is also considered that the UNIFAC groups, which constitute the anionic and cationic species, are the same as those of the zwitterion.

Accordingly, only new charged groups are defined to accurately describe the zwitterions in the solution: a new group COO^{-} present in all amino acids and peptides studied, the CNH_3^{+} group for the linear amino acids or peptides, and the group CNH_2^{+} for the cyclic amino acids proline and hydroxyproline. The group CO was also defined to represent the peptide bonding. Table 5.1 summarizes the new groups and subgroups defined, as well as the UNIFAC size parameters (R_k and Q_k), which are determined using Bondi volume and area parameters (Bondi, 1968).

The subgroups that compose all amino acids and peptides (their zwitterionic form) studied are shown in Table 5.2, while their structural formulas are given in Appendix D.

The interaction parameters between the different groups present in the solution are then possible to estimate using activity coefficient data as discussed in the next section.

Table 5.1 New UNIFAC group size parameters.

Group	Subgroup	R_k	Q_k
COO^-	COO^-	1.3013	1.224
CNH_3^+	$CH_2NH_3^+$	1.3692	1.236
	$CHNH_3^+$	1.1417	0.924
CNH_2^+	$CH_2NH_2^+$	1.2070	0.936
CO	CO	0.7713	0.640

Table 5.2 Subgroups of the amino acids and peptides on the zwitterionic form.

Substance	Subgroups
Alanine	CH_3, COO^-, $CHNH_3^+$
α-Amino n-butyric acid	CH_3, CH_2, COO^-, $CHNH_3^+$
α-Amino n-valeric acid	CH_3, $2CH_2$, COO^-, $CHNH_3^+$
Glycine	COO^-, $CH_2NH_3^+$
Hydroxyproline	CH_2, $2CH$, OH, COO^-, $CH_2NH_2^+$
Proline	$2CH_2$, CH, COO^-, $CH_2NH_2^+$
Serine	CH_2, OH, COO^-, $CHNH_3^+$
Threonine	CH_3, CH, OH, COO^-, $CHNH_3^+$
Valine	$2CH_3$, CH_2, COO^-, $CHNH_3^+$
Alanylalanine	$2CH_3$, $CHNH$, COO^-, $CHNH_3^+$, CO
Alanylglycine	CH_3, CH_2NH, COO^-, $CHNH_3^+$, CO
Glycylalanine	CH_3, $CHNH$, COO^-, $CH_2NH_3^+$, CO
Glycylglycine	CH_2NH, COO^-, $CH_2NH_3^+$, CO
Triglycine	$2CH_2NH$, COO^-, $CH_2NH_3^+$, $2CO$

5.2.3 Correlation and Prediction of Activity Coefficients

Hutchens (1976) compiled the molality scale unsymmetric activity coefficient data of amino acids and small peptides in pure water at 25 °C. The original measurements on osmotic coefficients and the subsequent conversion to activity coefficients were made by Smith and Smith (1937; 1940a,b), Hutchens et al. (1963), and Ellerton et al. (1964). Relevant information from the experimental data collected is shown in Table 5.3.

Table 5.3 Experimental data used for parameter estimation.

Substance	Number of Experimental Data Points	Maximum Molality	γ^* range
Alanine	7	1.86	1.005-1.045
α-Amino n-butyric acid	7	2.00	1.011-1.165
α-Amino n-valeric acid	5	0.65	1.022-1.072
Glycine	10	3.11	0.960-0-.738
Hydroxyproline	7	2.00	1.000-1.026
Proline	15	7.30	1.019-2.004
Serine	11	4.00	0.951-0.603
Threonine	7	2.00	0.989-0.944
Valine	3	0.50	1.030-1.076
Alanylalanine	5	1.00	0.982-1.035
Alanylglycine	5	1.00	0.931-0.855
Glycylalanine	5	1.00	0.935-0.855
Glycylglycine	6	1.50	0.911-0.689
Triglycine	2	0.30	0.851-0.804

5.2.3.1 Parameter Estimation

To estimate the new UNIFAC interaction parameters between groups (a_{nm}) a modified Levenberg-Marquardt method (Levenberg, 1944; Marquardt, 1963) was used to minimize the following objective function (OBJ):

$$OBJ = \sum_{l=1}^{N_{data}} \left(\gamma_{AA^{\pm}}^{*,calc} - \gamma_{AA^{\pm}}^{*,\exp} \right)_l^2 \tag{5.27}$$

where $\gamma_{AA^{\pm}}^{*}$ refers to the zwitterion molal unsymmetric activity coefficient, N_{data} to the number of experimental data points, and *calc* and *exp* mean calculated values according to the model and experimental, respectively.

An algorithm of the method used during the minimization process is presented in Figure 5.2, where the different convergence criteria used are shown. In fact, for the first iteration it is assumed ideal solution behaviour to solve the chemical equilibrium equations and, in this way, determine the composition of the system. At this calculated composition, the UNIFAC interaction parameters are obtained by minimization of the objective function. The chemical equilibrium is solved again with the new activity coefficients, and the whole process is repeated until no change in the UNIFAC interaction parameters is observed.

Seventeen data points available for alanine and glycine (Hutchens, 1976) were used to estimate four energy parameters between the groups H_2O, COO^- and $CHNH_3^+$: a_{H_2O,COO^-}, $a_{H_2O,CHNH_3^+}$, a_{COO^-,H_2O} and $a_{CHNH_3^+,COO^-}$ The determination of the interaction parameters between the new above-mentioned groups and the OH group was carried out using the data for serine (Hutchens, 1976). In this case, only two parameters were estimated since the best results were obtained when the interaction parameters for OH/COO^- and $OH/CHNH_3^+$ were set equal to the interaction parameters COO^-/OH and $CHNH_3^+/OH$, respectively.

The experimental data for proline and hydroxyproline were regressed together to estimate the parameters $a_{OH,CHNH_2^+}$, $a_{H_2O,CHNH_2^+}$, $a_{CHNH_2^+,CH_2}$ and $a_{CHNH_2^+,H_2O}$. The interaction parameters $a_{H_2O,CHNH_2^+}$ and $a_{CHNH_2^+,H_2O}$ were set equal during the calculations.

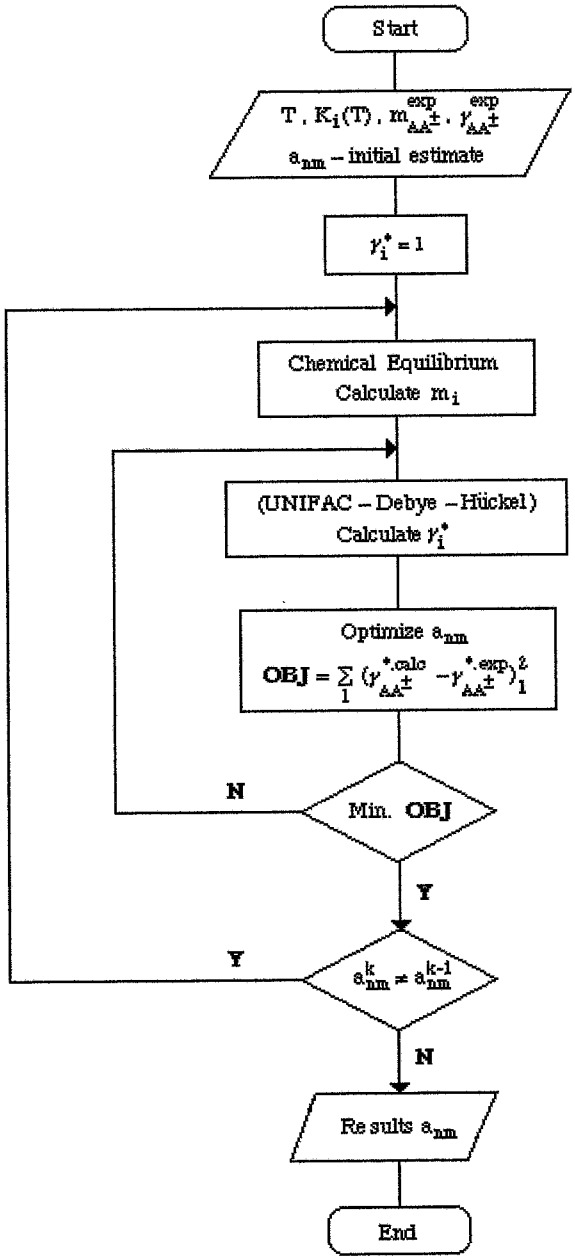

Figure 5.2 Algorithm used in the minimization process.

Finally, the minimization process applied to the available experimental data for alanylalanine and glycylalanine allowed the estimation of the group parameters $a_{H_2O,CO}$, $a_{CNH,CHNH_3^+}$, $a_{CNH,CO}$, $a_{CHNH_3^+,CNH}$ and a_{CO,H_2O}.

All the other relevant parameters were fixed. They were all given the same value (5000), because it turned out during the minimization that this value gave the best representation of the activity coefficients for the studied systems.

5.2.3.2 Results and Discussion

Table 5.4 presents the new estimated interaction parameters between groups for the UNIFAC model. Figures 5.3 and 5.4 show the good quality of the correlations.

Table 5.4 Group interaction parameters (K).

	CH_2	OH	H_2O	CNH	COO^-	CNH_3^+	CNH_2^+	CO
CH_2	0.0	986.5[a]	1318[a]	255.7[a]	5000	5000	5000	5000
OH	156.4[a]	0.0	353.5[a]	42.70[a]	-577.0	170.6	-572.4	n.a.[b]
H_2O	300.0[a]	-229.1[a]	0.0	168.0[a]	-1354	803.5	-114.3	93.03
CNH	65.33[a]	-150.0[a]	-448.2[a]	0.0	5000	-335.9	n. a.	-1142
COO^-	5000	-577.0	-568.9	5000	0.0	5000	5000	5000
CNH_3^+	5000	170.6	5000	-768.4	-2041	0.0	n. a.	5000
CNH_2^+	-536.5	5000	-114.3	n. a.	5000	n. a.	0.0	n. a.
CO	5000	n. a.	-680.0	5000	5000	5000	n. a.	0.0

[a]Values from the UNIFAC VLE tables (Hansen et al., 1991). [b]n.a.: not available.

Table 5.5 summarizes some of the information for both correlation and prediction, and a comparison is given with the results of Chen et al. (1989), Gupta and Heidemann (1990), and Peres and Macedo (1994). The root mean square deviation (*rmsd*) is calculated in accordance to:

$$rmsd\ (\%) = \sqrt{\frac{\sum_{i=1}^{N_{data}} \left(\gamma_{AA^{\pm}}^{*,calc} - \gamma_{AA^{\pm}}^{*,\exp}\right)_i^2}{N_{data}}} * 100 \qquad (5.28)$$

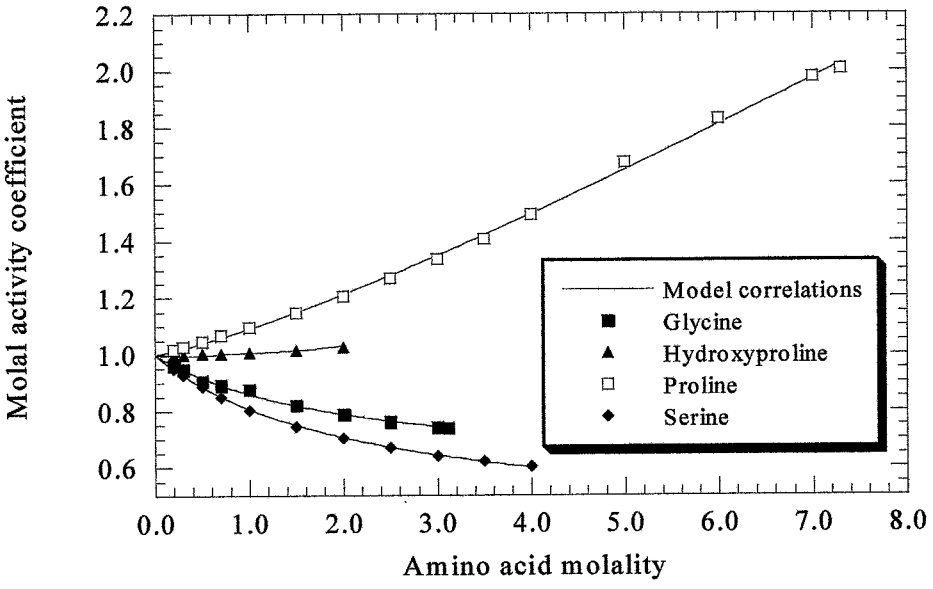

Figure 5.3 *Experimental (Hutchens, 1976) and calculated values for the activity coefficients of different amino acids in water at 298.15 K.*

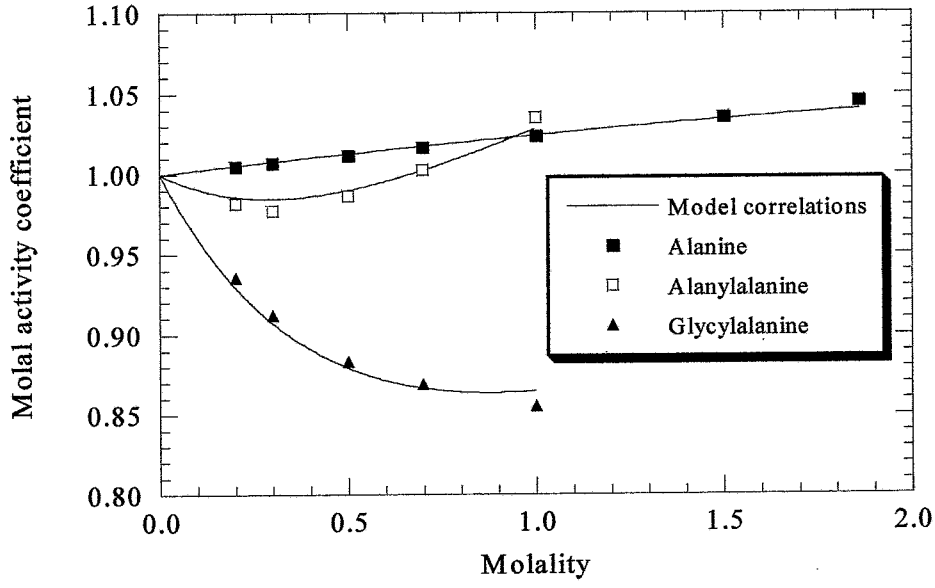

Figure 5.4 *Experimental (Hutchens, 1976) and calculated values for the activity coefficients of alanine and some peptides in water at 298.15 K.*

Table 5.5 *Comparison (rmsd values in percentage) for different models concerning the correlation and/or prediction of the activity coefficients.*

Substance	This Work	Chen et al. (1989)	Gupta and Heidemann (1990)	Peres and Macedo (1994)
Alanine	0.19	0.04	8.97	0.02
Glycine	0.60	2.07	4.20	0.57
Hydroxyproline	0.39	0.36	0.06	0.11
Proline	1.21	1.30	3.01	1.36
Serine	0.24	2.80	3.32	0.18
Alanylalanine	0.52	2.04	—	0.09
Glycylalanine	0.59	2.44	—	0.13
α-Amino n-butyric acid	17.87[a]	0.32	17.34[a]	0.51
α-Amino n-valeric acid	16.40[a]	—	—	0.04
Threonine	26.12[a]	0.70	13.78[a]	0.09
Valine	16.43[a]	4.47	12.15[a]	0.04
Alanylglycine	28.22[a]	2.92	—	0.35
Glycylglycine	17.06[a]	3.25	—	0.05
Triglycine	10.00[a]	0.67	—	0.0002
Average Values	0.53 18.87[a]	1.80	3.91 14.42[a]	0.25

[a]Results from predictions.

The *rmsd* values for the correlation are quite satisfactory, and in the majority of the cases the deviations are even smaller than those calculated by Chen et al. (1989), who correlated two parameters for each amino acid or peptide. The other correlation model (Peres and Macedo, 1994), with the same number of parameters of the Chen model (Chen et al., 1989), is indeed much more accurate (*rmsd* average 0.25%), but presents the same order of magnitude of this new UNIFAC model. Moreover, this new model is able to make predictions, since other amino acids may be built from the groups defined as will be discussed in section 5.3.

Concerning the UNIFAC based model by Gupta and Heidemann (1990), the results seem to deviate more from the experimental data than those obtained in this work even if, for the same amino acids, the same number of parameters were regressed. In fact, while for the correlations much better results are obtained, for the predictions, they are about the same order of magnitude. Like has already been stated, Gupta and Heidemann (1990) defined very large groups, such as the glycine and the proline molecules. These are not small units to build other amino acid molecules and so flexibility is lost. Choosing glycine as a group, the extension of the model to peptides is forbidden.

Figure 5.5 shows, the predicted curves for the activity coefficients of α-amino n-butyric acid and glycylglycine. The prediction results require some attention: the *rmsd* values calculated are much higher than the ones obtained for correlation, though they are about the same order of magnitude of the values obtained by Gupta and Heidemann (1990).

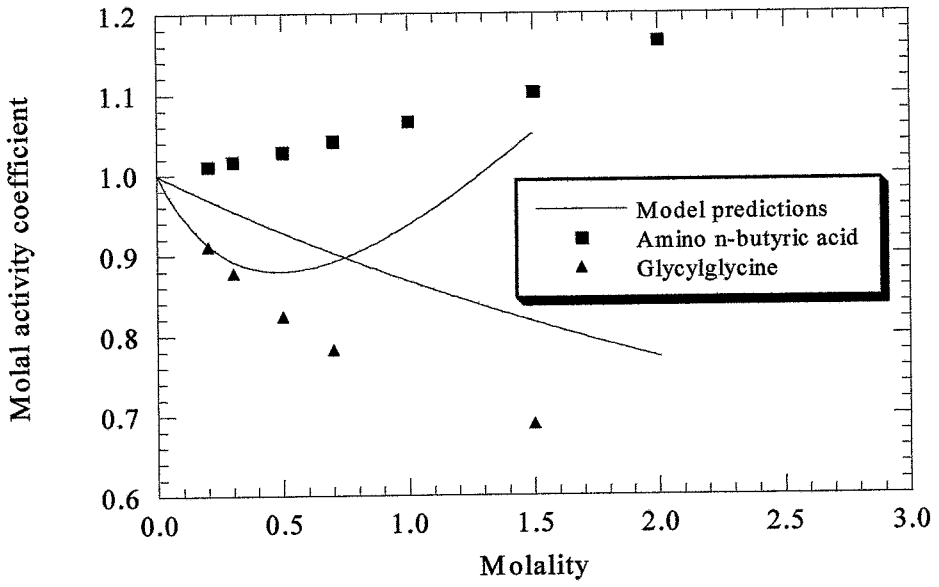

Figure 5.5 *Comparison of the model predictions with the experimental activity coefficients (Hutchens, 1976).*

For the prediction of the activity coefficients of valine, α-amino n-butyric acid and α-amino n-valeric acid an incorrect slope was always found. The calculated molal activity coefficient decreases with rising molality, while the data show the opposite trend.

An explanation for this might come from the interaction between the groups CH_2 and H_2O: the interactions between methyl groups and the new charged groups are not important, since all parameters have high values. The three amino acids above-mentioned are obtained from alanine by addition of methyl groups (see Table 5.2) and the introduction of CH_2/H_2O interaction parameters is very important, suggesting the study of the effect of the addition of methyl groups on the activity coefficients of hypothetical mixtures of n-alkanes/water. Surprisingly, a deep decrease of the molal activity coefficients with molality is observed. In some way, these results tend to show that the interaction parameters between CH_2 and H_2O (Hansen et al., 1991) are not the best to represent the behaviour of solutions of this kind. Moreover, difficulties arise in getting good correlations using amino acids with long hydrocarbon chains, which support this point. However, to maintain the group-contribution concept, no re-evaluation of that pair of parameters was done.

Avoiding this problem, Kuramochi et al. (1996), divided the CH_2 group in two new groups $\alpha - CH$ and $sc - CH_2$ (side chain CH_2). As a consequence, a better representation of the activity coefficients of amino acids with larger hydrocarbon chain was achieved, and the predictions have much lower *rmsd's* (average 2.86%) than those obtained in this work or by Gupta and Heidemann (1990).

However, the number of regressed parameters duplicates relatively to the model proposed here, without getting better correlations (0.74% average *rmsd*). Moreover, since the chemical equilibrium is not taken into account, the study of the pH influence on the solubilities of amino acids, like presented in section 5.4, is disregarded.

5.3 Temperature Dependency of the Solubilities

Some studies and compilations report experimental amino acid solubilities in water at temperatures from 273.15 up to 348.15 K. However, these solubilities cannot be extrapolated with confidence using polynomial fits of the data (Amend and Helgeson, 1997).

Thus, in this section a procedure to represent the solubility of amino acids in water at different temperatures using the developed activity coefficient model is presented. It should be mentioned that, due to the lack of experimental data on the solubilities of peptides in water, in this study only amino acids are considered.

5.3.1 Proposed Equation for the Correlation

The solubility equation used in Chapter 4 can also be used for the correlation or prediction of the solubilities of amino acids in water. Most amino acids, however, decompose before reaching the melting temperature and the calorimetric properties expressed there are not measurable or are unavailable. Thus, in this work the solubility data is represented regressing the thermodynamic solubility constant of equation 5.6 in the form:

$$\ln K_s = \alpha + \frac{\beta}{T} + \lambda \ln T \tag{5.29}$$

where α, β and λ are temperature-independent parameters.

It should be noticed that the equilibrium constant K_s is the combination of the equilibrium constants from equations 5.1 and 5.2, k_s and K_D, respectively. The small difference in standard states between reaction 5.1 (system pressure) and reaction 5.2 (standard pressure) is then incorporated into K_s, since it is an adjustable parameter.

5.3.2 Parameter Estimation

Hutchens (1976) compiled the solubilities of amino acids between 273.15 and 373.15 K. However, original experimental data from Dalton and Schmidt (1933), and Dunn et al. (1933) cover only the temperature range between 273.15 and 348.15 K. The known values of solubility above this temperature were obtained by extrapolation of the smoothed curve.

To regress the coefficients of equation 5.29, only experimental and interpolated values of solubilities between 273.15 and 348.15 K were used. The objective function used for this purpose was:

$$OBJ = \sum_{l=1}^{N_{data}} \left(S^{calc} - S^{\exp} \right)_l^2 \tag{5.30}$$

being S the solubility in g/kg of water.

The computer program developed for this purpose, like for the regression of the molal activity coefficients, involves an iterative procedure because the equilibrium composition of the system depends on the K_s value, which in turn is composition dependent.

5.3.3 Results and Discussion

The regressed parameters α, β and λ are listed in Table 5.6. This table also shows a comparison between the *rmsd* values from this work and those presented by Peres and Macedo (1994). The *rmsd*'s calculated by those authors are, in average, better than those obtained in this work, 0.62% and 1.01%, respectively. However, since a group-contribution model is used in this formulation it was possible to make calculations for some amino acids, for which no activity coefficient data is available, while Peres and Macedo (1994), with the UNIQUAC model for electrolytes, could not. The subgroups that build those amino acids are listed in Table 5.7.

Table 5.6 Solubility constants of amino acids in water.

Amino Acid	Maximum Molality	α	β(K)	λ	*rmsd** (%)	
					This Work	Peres and Macedo (1994)
d-Alanine	3.20	-25.32	1006	3.968	0.35	0.06
dl-Alanine	3.58	-13.60	318.2	2.318	0.40	0.14
Glycine	7.25	114.8	-5558	-16.72	1.62	0.29
l-Hydroxyproline	4.12	-43.90	2520	6.410	0.44	0.07
l-Isoleucine	0.29	-44.31	1663	6.531	0.01	—
dl-Isoleucine	0.35	-121.7	4709	18.26	0.01	—
l-Leucine	0.29	-117.5	4886	17.42	0.03	—
dl-Leucine	0.17	-170.8	6687	25.57	0.02	—
dl-Norleucine	0.22	-135.6	4934	20.47	0.01	—
l-Proline	21.79	-182.3	9771	26.91	1.68	0.27
l-Serine	5.63	664.4	-30250	-98.65	8.90	2.82
dl-Serine	1.63	118.7	-7265	-16.71	0.39	0.64
l-Valine	0.54	-55.99	2287	8.319	0.02	0.10
dl-Valine	1.00	-62.73	2486	9.412	0.26	1.22

* $rmsd\ (\%) = \sqrt{\sum_{i=1}^{N_{data}} \left(S^{calc} - S^{exp}\right)_i^2 \Big/ N_{data}} * 100$

Table 5.7 Subgroups of some amino acids for the solubility study.

Substance	Subgroups
Isoleucine	$2CH_3$, CH_2, CH, COO^-, $CHNH_3^+$
Leucine	$2CH_3$, CH_2, CH, COO^-, $CHNH_3^+$
Norleucine	CH_3, $3CH_2$, COO^-, $CHNH_3^+$

The quality of the regression can be seen in Figures 5.6 and 5.7 for some amino acids. These figures also show the solubilities predicted with this model at temperatures above 348.15 K and the extrapolated solubilities from the experimental data given by Hutchens (1976). Some results related with those predictions are shown in Table 5.8, and a comparison with the values obtained by Peres and Macedo (1994) is presented.

It is possible to observe big discrepancies between predicted and extrapolated values for glycine, dl-serine, and dl-valine at 373.15 K, but on average the errors are not large (< 5.8% with the model suggested here and < 3.8% for the UNIQUAC model). For glycine the model predicts a maximum solubility (Figure 5.6), while extrapolated values show almost a linear increase in the solubility up to 373.15 K. It would be nice to see what is the experimental curve in that zone.

For l-isoleucine, l-serine, and l-valine such a comparison is not presented since the available experimental data for the solubilities only attains a maximum temperature of 313.15 K.

Although the results in general are good, some aspects deserve attention:

- Extrapolations had to be made both on temperature and composition. The temperature range is now between 273.15 and 373.15 K, while the UNIFAC parameters were estimated from experimental data at 298.15 K only. As regards composition, for almost all amino acids, maximum molality (Table 5.6) is now much higher than the maximum molality for the experimental data on activity coefficients (Table 5.3). This may explain the difficulties in obtaining accurate results for glycine and l-proline amino acids.

- The model for the activity coefficients is based on data for the dl forms of the amino acids, but was used indifferently to d, l and dl forms since UNIFAC does not differentiate optical isomers.

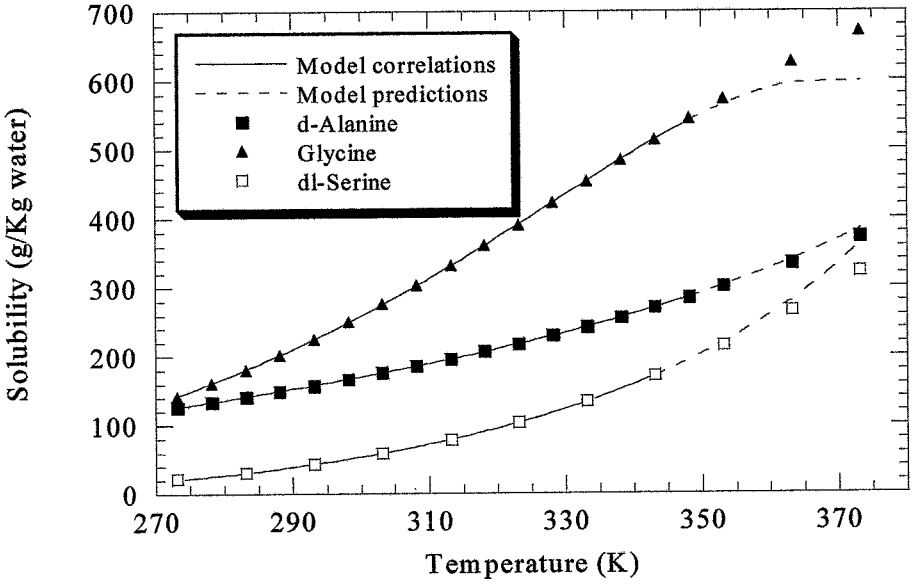

Figure 5.6 *Amino acids solubility in water: correlation and prediction curves. Comparison with experimental data from Dalton and Schmidt (1933) and the extrapolated values from Hutchens (1976).*

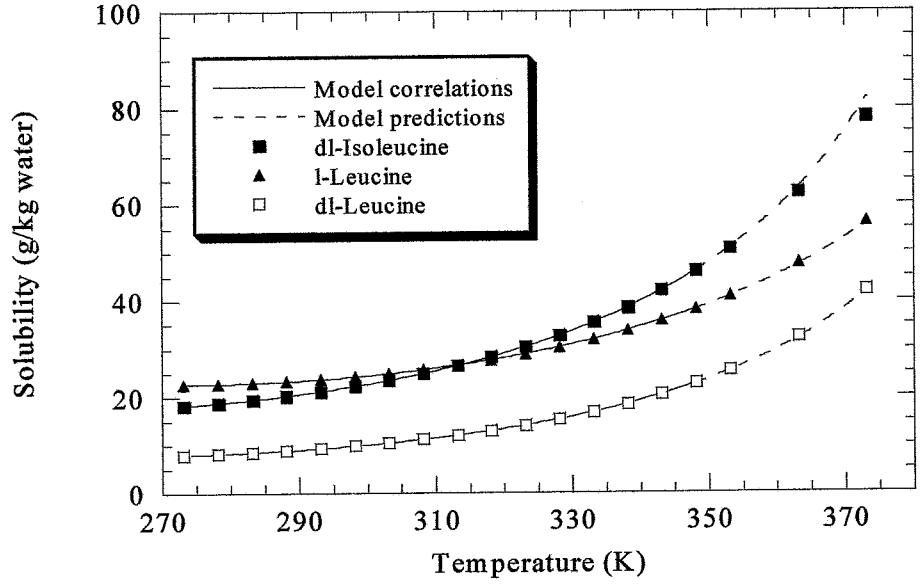

Figure 5.7 *Amino acids solubility in water: correlation and prediction curves. Comparison with experimental data from Dalton and Schmidt (1933) and the extrapolated values from Hutchens (1976).*

Table 5.8 *Comparison between the extrapolated (S^{ext}) and predicted solubilities (S^{calc}), with the UNIFAC (this work) and the UNIQUAC (Peres and Macedo, 1994) models, in g/kg water at 373.15 K.*

Amino Acid	S^{ext}	This Work		Peres and Macedo (1994)	
		S^{calc}	*Error** (%)	S^{calc}	*Error** (%)
d-Alanine	373.0	383.8	-2.92	375.8	-0.75
dl-Alanine	440.4	454.9	-3.29	441.2	-0.18
Glycine	671.7	597.9	10.99	651.7	2.98
l-Hydroxyproline	706.9	722.1	-2.15	703.7	0.45
dl-Isoleucine	78.02	81.93	-5.01	-	-
l-Leucine	56.38	55.83	0.97	-	-
dl-Leucine	42.06	41.73	0.78	-	-
dl-Norleucine	52.29	53.46	-2.24	-	-
l-Proline	3355	3409	-1.61	3369	-1.02
dl-Serine	322.4	363.0	-12.59	364.2	-12.96
dl-Valine	188.1	227.2	-20.79	177.3	5.74

* $Error\ (\%) = 100 * \left(S^{ext} - S^{calc}\right) / S^{ext}$

5.4 pH Influence on the Solubility of the Amino Acids

The main feature of this model is the ability to predict the solubilities of amino acids in water as a function of the pH, which it is not possible with the UNIFAC model by Kuramochi et al. (1996). Due to the limitations discussed before, the model suggested by Gupta and Heidemann (1990), should be used with caution.

This study is intimately related with the consideration of equilibrium reactions 5.3 to 5.6 in the solution. Thus, the model activity coefficient together with the results from solubility correlation were used to predict solubilities at different pH conditions.

Figure 5.8 shows a comparison between the experimental data for the solubilities of glycine at 298.15 K at different pH values (Needham et al., 1971; Carta, 1998) with predictions from the model. The predictions show a good agreement with the experimental results obtained by Needham et al. (1971), but for the experimental data reported by Carta (1998) the deviations are higher. However, even at the isoelectric point (around $pH = 6.1$) the result by Carta (1998) is below the experimental value, commonly accepted, for the solubility of glycine in water at 298.15 K.

A better prediction is obtained for the solubility of l-leucine in water at 298.15 K, as presented in Figure 5.9. In this case the solubility value, at the isoelectric point, measured by Carta (1998) is much more in agreement with the values already available in the literature (Hutchens, 1976).

The quality of the predictions are better than expected, that is, during the experimental work it was necessary to add a strong electrolyte (acid or basic) to fix the pH at a required value, and of course the electrolyte gives rise to new important interactions between the molecules, as can be understood from the works of Schrier and Robinson (1974), Briggs et al. (1974), Fiol et al. (1995), Carta (1998), and Pradhan and Vera (1998), among others. Curiously, the values reported by Carta (1998) for the glycine solubility in water, are for solutions without the addition of an electrolyte, while the data that better agree with the predicted curve from Needham et al. (1971) were obtained adding HCl or NaOH.

Figure 5.10 displays the influence of the addition of different electrolytes on the solubility of dl-alanine (Pradhan and Vera, 1998). One set refers to the addition of KOH or HNO_3 and for the other set the electrolytes used are NaOH or HCl. It is shown that the effect of the different ions on the solubility is small in the pH range studied.

A good agreement for the proposed model at low pH values is observed, but not at high pH values. It seems that the model predicts solubility values extremely high in that zone. Though the results clearly disagree, it is important to refer that the same authors report a solubility value of 168.5 g/kg water in neutral solution, but a much higher one (2490.2 g/kg water) in a solution 8M in KOH.

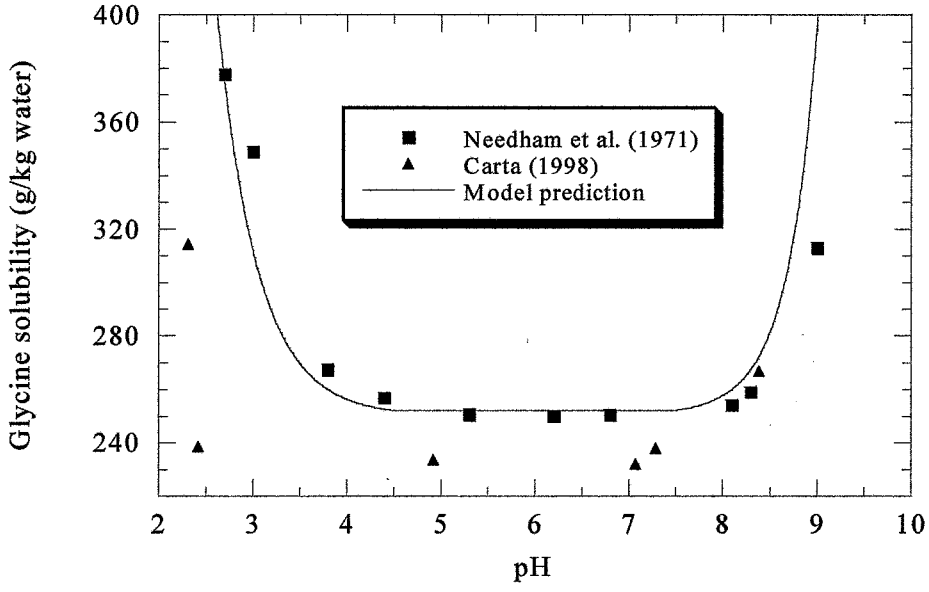

Figure 5.8 *Experimental and predicted values for the influence of pH on the solubility of glycine at 298.15 K.*

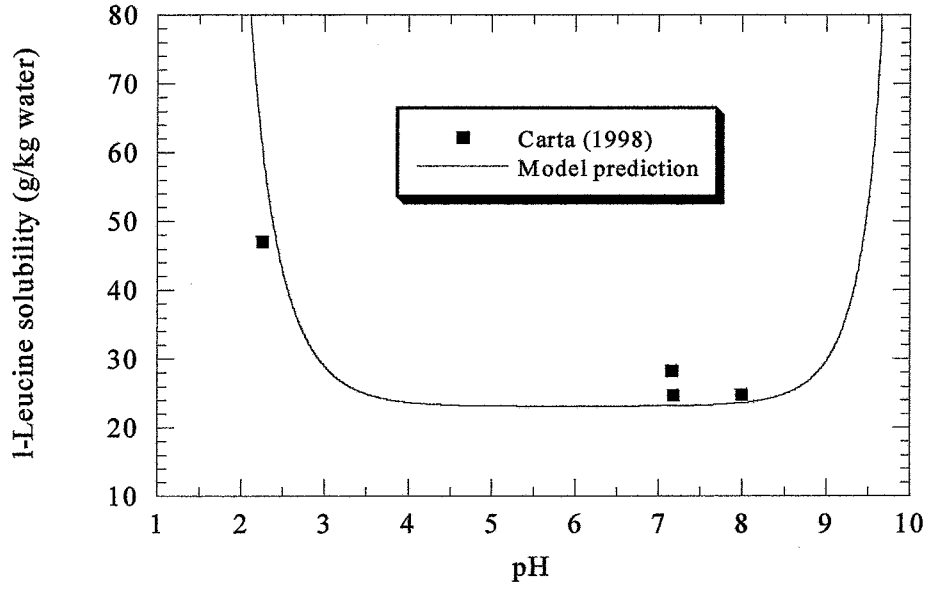

Figure 5.9 *Experimental and predicted values for the influence of pH on the solubility of l-leucine at 298.15 K.*

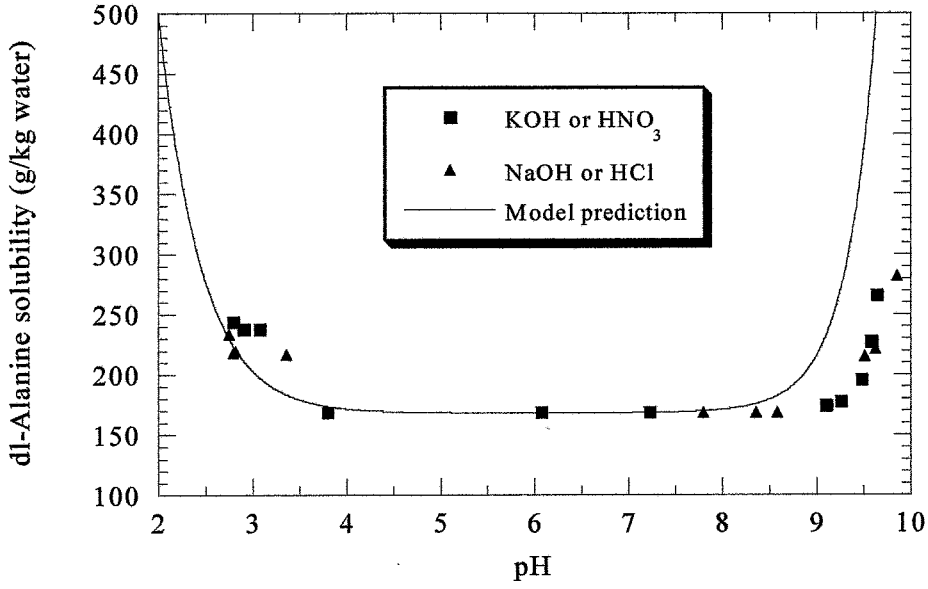

Figure 5.10 *Effect of acids and bases on the solubility of dl-alanine at 298.2 K: experimental results (Pradhan and Vera, 1998) and model prediction.*

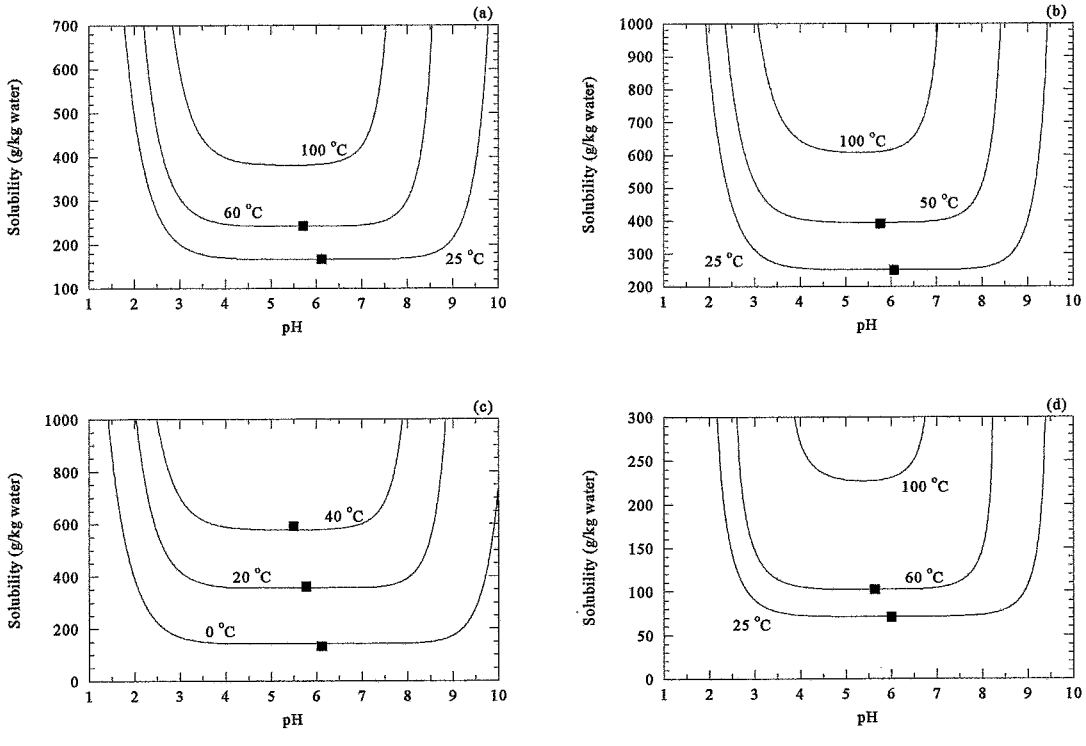

Figure 5.11 *Predicted solubility of different amino acids as function of pH and temperature: (a) d-alanine (b) glycine (c) l-serine (d) dl-valine.*

In general the results may be considered good. Figure 5.11 shows predicted curves of solubility as a function of *pH* at different temperatures for some amino acids. They are similar to the experimental curves obtained by Dalton et al. (1930) for diiodotyrosine at three temperatures, showing the same type of behaviour as we change from one temperature to another. It is also possible to identify the predicted minimum solubility at the isoelectric point with the invariant solubility bands on both sides of it. The predicted bands at 25 °C are inside the range of 2-3 *pH* units on either side of the isoelectric point, as indicated in the works of Needham et al. (1971) and Zumstein and Rousseau (1989).

5.5 Conclusions

A new model combining chemical equilibria with an UNIFAC-Debye-Hückel approach to describe physical equilibria has been developed for the correlation and prediction of activity coefficients of amino acids or peptides in water. New charged groups have been defined taking into account the charges in the zwitterionic, the anionic and the cationic species of amino acids. The results achieved for correlation are in a very good agreement with experimental data. Regarding predictions, the model must be used with caution since the average *rmsd* is large.

The model provides good results for the correlation of the solubility, and a comparison between calculated solubilities and the extrapolated values from the experimental curves shows good agreement.

Since studies of *pH* influence on the solubility are extremely dependent on the correlation of solubilities, care must be taken at temperatures higher than 348.15 K. However, estimated bands of constant solubility at different temperatures are very reasonable for all amino acids studied, and the comparisons done between the predicted curves and the available experimental data at 298.15 K are very satisfactory.

Finally, it is worthwhile stressing a point already emphasized: the available data are scarce and most of it old, which may introduce some uncertainties in the obtained results. Therefore, experimental work to verify and improve the results is extremely welcome.

List of Symbols

a	activity
a	distance of closest approach, m
a	UNIFAC interaction parameter, K
A	Debye-Hückel parameter, $kg^{0.5}mol^{-0.5}$
aq	aqueous solution
B	Debye-Hückel parameter, $kg^{0.5}mol^{-0.5}m^{-1}$
f	rational activity coefficient
G	Gibbs energy
K_D	chemical equilibrium constant, equation 5.2
k_s	equilibrium constant, equation 5.1
K_s	solubility product of an amino acid or peptide, equation 5.6
K_w	ionic product of water
K_1	chemical equilibrium constant, equation 5.3
K_2	chemical equilibrium constant, equation 5.4
m	molality, $molkg^{-1}$
N_{data}	number of experimental data points
q	surface area parameter of a species
Q	surface area parameter of a group
r	van der Waals volume parameter of a species
R	van der Waals volume parameter of a group
s	solid state
S	solubility, g/kg water
T	absolute temperature, K
x	mole fraction in the liquid phase
X	fraction parameter of a group

Greek Letters

α	parameter in equation 5.29
β	parameter in equation 5.29
γ	molal activity coefficient
Γ	activity coefficient of a group

θ	area fraction of a group
Θ	area fraction of a molecule
λ	parameter in equation 5.29
ν	number of groups
τ	parameter according to equation 5.25
Φ	volume fraction of a molecule

Subscripts

DH	Debye-Hückel model
i	species or molecule
j	species or molecule
k	group
l	experimental point
m	group
n	group
UNIFAC	UNIFAC model
w	water

Superscripts

calc	calculated by the model
C	combinatorial
DH	Debye-Hückel model
exp	experimental
ext	extrapolated
E	excess property
i	species or molecule
k	iteration
m	molal scale
R	residual
UNIFAC	UNIFAC model
$*$	unsymmetric
$+$	cation
$-$	anion

$\pm$	zwitterion

Abbreviations

AA	amino acid or peptide
OBJ	objective function
pI	isoelectric point
rmsd	root mean square deviation

Chapter 6

CONCLUSIONS

6. Conclusions

6.1 Main Conclusions

Thermodynamics of electrolyte solutions is not a minor extension of non-electrolyte thermodynamics. The fundamental question about their degree of dissociation and phenomena like ion-association or solvation leaves some doubts about the total number of different species in solution. It is then common to classify the electrolytes as strong, when it is assumed that they are completely dissociated into anions and cations, and weak electrolytes, when the chemical equilibrium plays an important role.

As fundamental concepts, the different concentration scales used have been focused, being the molality and mole fraction scales the most used. The standard sates, which usually are different for solvents and for solutes have also been analysed, leading to the unsymmetric convention where the activity coefficients of all components go to unity at infinite dilution or the symmetric convention where that value is attained in the case of pure component. Special attention has been given to the very important conversions between the several possible activity coefficients obtained for those concentration scales and standard states.

The activity coefficients of the individual ions are not measurable quantities. Thus, the definition of mean ionic activity coefficients was introduced for electrolytes. This coefficient gives real indication of the deviation from ideality even at infinite dilution, while the solvent activity does not, leading to the introduction of the osmotic coefficient concept.

In fact, even at high distances, there are strong interactions between ions. The electrostatic forces are well represented at infinite dilution through the Debye-Hückel theory. However, as the ionic concentration rises extensions of this theory are required and some examples have been presented.

Pitzer's model is the most successful model for aqueous solutions, while for mixed solvent systems several semi-empirical models have been reviewed. Absolute comparisons between them are very difficult to make because the models contain different number and type of interaction parameters that may change from system to system. However, these models correlate osmotic and mean ionic activity coefficients in aqueous systems within 1 to 2% and have the important characteristic of being easily extended to mixed solvent solutions.

A large amount of both experimental and modelling work has been carried out for VLE in mixed solvent systems. Much different is the case concerning LLE or SLE. The importance of the last in the understanding of the salt effect in VLE and the stringent test of those models in their capabilities to represent different types of equilibria lead to the establishment of a project for salt solubilities in mixed solvents.

Due to the results presented for the correlation or/and prediction of VLE in mixed solvent systems, and of solubilities in water, the UNIQUAC based models are suitable for the study of salt solubility in mixed solvents.

The simple apparatus designed for the measurement of salt solubilities in mixed solvents using an analytical method proved to be very successful; high precision and accurate results were obtained and generally the solubilities are reproducible when compared to the few values reported in the literature.

The systematized experimental study implemented in this work is an important contribution for the fulfilling of the great demanding of salt solubility in non-aqueous and mixed solvent systems; a high number of new experimental solubilities have been measured for the salts NaCl, KCl, NaBr, KBr, in the pure solvents water, methanol, ethanol, and in the mixed solvents water/methanol, water/ethanol and methanol/ethanol at different temperatures.

The number of experimental measured solubilities which, duplicates the number of the experimental data points available and, the temperature and composition ranges covered in the different studied systems, together with other experimental thermodynamic properties or equilibrium for this kind of systems allow the establishment of a large and reliable database.

That database is used for the development of thermodynamic models for correlation and prediction of the solubilities.

A new formulation for the calculation of the solubility of salts in pure and mixed solvents is presented. It involves the symmetric convention of normalization of the activity coefficients, for all species, and the mole fraction on ionized basis. In this way, a considerable simplification is introduced since the salt solubility product can be evaluated in terms of its thermodynamic properties such as the melting temperature, the enthalpy of fusion, and the change of heat capacity, between the liquid and solid state.

Two models are proposed to correlate and/or predict the salt solubilities, the UNIQUAC + Pitzer-Debye-Hückel (UNIQUAC + PDH) model and the UNIQUAC model with linear temperature dependent parameters between the salt and the solvents.

Concerning the water/salt systems it is possible to conclude that the UNIQUAC model can describe better the temperature influence on the salt solubility, but presents much higher deviations than the UNIQUAC + PDH model in the representation of osmotic coefficients. This confirms the need of a Debye-Hückel expression type to account for the electrostatic forces in electrolyte systems, at least for the dilute salt region.

Both models correlate satisfactorily and with similar accuracy the solubility of salts in mixed solvents, but it is clearly shown that temperature and electrostatic effects are both very important in this type of equilibrium calculations. The average deviation is around 7.5 %, but the UNIQUAC + PDH model shows a more reliable description for the water/methanol and water/ethanol solvent mixtures.

However, if the purpose is to correlate the salt solubility diagram of a specific system, the UNIQUAC model is preferred due to the better results obtained and to its simplicity.

The Setschenow empirical equation, using the same number of parameters as for the two proposed models, gives poorer representation of the solubilities of salts in mixed solvents.

The models give better results for salts that do not present hydrated phases. Indeed, for the systems involving NaBr, which forms a dihydrated solid phase in water at temperatures lower than 323.98 K, the results are not so good even if the average *AAD* are low. The different solubility trends in systems involving the salt NaBr are difficult to describe, suggesting a study of the different solid phases that may appear.

These models and this methodology are a valuable tool for the correlation and prediction of salt solubility in mixed solvents. The predictions obtained for the solubilities of KCl and KBr in the water/methanol/ethanol mixed solvent are motive of stimulation for further developments.

Concerning the study on weak electrolyte solutions, a new model combining chemical equilibria with a UNIFAC-Debye-Hückel approach to describe physical equilibria has been developed for the correlation and prediction of activity coefficients of amino acids or peptides in water. New charged groups have been defined taking into account the charges in the zwitterionic, the anionic and the cationic species of amino acids. The results achieved for correlation are in a very good agreement with experimental data. Regarding predictions, the model must be used with caution since the average *rmsd* is not very low.

The model provides good results for the correlation of the solubility, and a comparison between calculated solubilities and the extrapolated values from the experimental curves shows good agreement.

Since studies of *pH* influence on the solubility are extremely dependent on the correlation of solubilities, care must be taken at temperatures higher than 348.15 K. However, estimated bands of constant solubility at different temperatures are very reasonable for all amino acids studied, and the comparisons done between the predicted curves and the available experimental data at 298.15 K are very satisfactory.

The good obtained results suggest that the model can be applied for simulation processes where the influence of *pH* and temperature are fundamental variables.

6.2 Suggestions for Future Work

Despite the large effort developed in this work for the measurement of the salt solubility in non-aqueous and mixed solvents, which contributed to fill the gap found in this field, it turns out the need to concentrate efforts in the experimental work in this area.

The study of the solubilities of the salts LiCl and LiBr, in methanol, ethanol and their mixed solvents is strongly recommended. The extension then, to other solvents that for some salt concentration values give rise to the appearance of phase instability, and consequently, to the formation of two liquid phases, as well as the measurement of the solubilities for mixed electrolytes in mixed solvents, is an open way.

Those measurements suggested are important to allow progresses into a better founded parameter table for solid-liquid calculations, as well as to test more deeply the models capabilities and the procedure suggested in this work. The challenge is to develop a group contribution method for solid-liquid equilibrium. Also, the separation of biomolecules involves frequently the use of salts and alcohols and would be of most importance to have more experimental information available for this kind of systems.

Experimental data is also needed to support some conclusions in the study of the solubility of amino acids. The recent data published in the literature for the pH influence on the solubility confirmed in an excellent way the prediction capabilities of the proposed model, but experimental measurements at temperatures higher than 348.15 K and at different pH values would be very important.

Finally, it would be rather interesting the study, from experimental and theorethical points of view, of the solubility of amino acids in mixed solvents.

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APPENDICES

A. Activity Coefficients for Different Concentration Scales

A.1 Introduction

In the following sections, the very important relations in the thermodynamic of electrolyte solutions, between the activity coefficients for different concentration scales, as presented in Table 2.2, are derived.

The derivations are based on the fact that: the chemical potential of a species i at a given composition depends only on the temperature and the pressure whatever concentration scale or normalization convention is adopted. Thus, it is possible to write:

$$\mu_i = \mu_i^{\bullet,x} + RT\ln\left(f_i^* x_i\right) = \mu_i^{\bullet,m} + RT\ln\left(\gamma_i^* m_i\right) = \mu_i^{\bullet,c} + RT\ln\left(y_i^* c_i\right) \qquad \text{(A.1)}$$

Also, it should be remembered that the reference state is chosen in such a way that, at infinite dilution of all ionic species, $\sum_{l=1}^{N_{solv}} \theta_l \to 0$, at all temperatures and pressures, $f_i^* = \gamma_i^* = y_i^* = 1$, where θ is the concentration scale adopted.

A.2 Relations Between f_i^* and γ_i^*

First, it is convenient to find a relation between $\mu_i^{\bullet,x}$ and $\mu_i^{\bullet,m}$. From equation A.1:

$$\mu_i = \mu_i^{\bullet,x} + RT\ln\left(f_i^* x_i\right) = \mu_i^{\bullet,m} + RT\ln\left(\gamma_i^* m_i\right) \tag{A.2}$$

or,

$$\frac{\mu_i^{\bullet,x} - \mu_i^{\bullet,m}}{RT} = \ln\left(\frac{\gamma_i^* m_i}{f_i^* x_i}\right) \tag{A.3}$$

From Table 2.1 it is possible to write one of the following equations:

$$\frac{x_i}{m_i} = \sum_{m=1}^{N_{solv}} x_m M_m \tag{A.4}$$

$$\frac{m_i}{x_i} = \sum_{l=1}^{N_{solu}} m_l + 1\Big/\sum_{m=1}^{N_{solv}} x_m' M_m \tag{A.5}$$

Taking the limit, when $\sum_{l=1}^{N_{solu}} x_l \to 0$ or $\sum_{l=1}^{N_{solu}} m_l \to 0$, then $\frac{m_i}{x_i} \to 1\Big/\sum_{m=1}^{N_{solv}} x_m' M_m$. Inserting this result into equation A.3, it is possible to obtain:

$$\frac{\mu_i^{\bullet,x} - \mu_i^{\bullet,m}}{RT} = \ln\left(1\Big/\sum_{m=1}^{N_{solv}} x_m' M_m\right) \tag{A.6}$$

Comparing equations A.3 and A.6:

$$\frac{\gamma_i^* m_i}{f_i^* x_i} = 1\Big/\sum_{m=1}^{N_{solv}} x_m' M_m \tag{A.7}$$

Equation A.7 can be rearranged in two ways:

$$\gamma_i^* = \frac{1}{\sum_{m=1}^{N_{solv}} x_m' M_m}\frac{x_i}{m_i} f_i^* \underset{\text{eq. (A.4)}}{\Uparrow} \frac{\sum_{m=1}^{N_{solv}} x_m M_m}{\sum_{m=1}^{N_{solv}} x_m' M_m} f_i^* \tag{A.8}$$

or,

$$f_i^* = \sum_{m=1}^{N_{solv}} x_m' M_m \frac{m_i}{x_i} \gamma_i^* \underset{\Uparrow\ eq.(A.5)}{=} \sum_{m=1}^{N_{solv}} x_m' M_m \left(\sum_{l=1}^{N_{solu}} m_l + 1 \Big/ \sum_{m=1}^{N_{solv}} x_m' M_m \right) \gamma_i^* = \left(\sum_{l=1}^{N_{solu}} m_l \sum_{m=1}^{N_{solv}} x_m' M_m + 1 \right) \gamma_i^* \tag{A.9}$$

Equations A.8 and A.9 are the desired expressions, relating the unsymmetric rational (f_i^*) and molal (γ_i^*) activity coefficients.

A.3 Relations Between γ_i^* and y_i^*

By analogy with the previous derivation:

$$\frac{\mu_i^{\bullet,m} - \mu_i^{\bullet,c}}{RT} = \ln\left(\frac{y_i^* c_i}{\gamma_i^* m_i} \right) \tag{A.10}$$

The equations relating m_i and c_i, as shown in Table 2.1, are:

$$\frac{m_i}{c_i} = \frac{1 + \sum_{l=1}^{N_{solu}} m_l M_l}{\rho} \tag{A.11}$$

$$\frac{c_i}{m_i} = \rho - \sum_{l=1}^{N_{solu}} c_l M_l \tag{A.12}$$

Taking the limit, when $\sum_{l=1}^{N_{solu}} m_l \to 0$ or $\sum_{l=1}^{N_{solu}} c_l \to 0$, then $\frac{c_i}{m_i} \to \rho_\circ$. Applying this to equation A.10:

$$\frac{\mu_i^{\bullet,m} - \mu_i^{\bullet,c}}{RT} = \ln \rho_\circ \tag{A.13}$$

Comparing eqs. A.10 and A.13:

$$\frac{y_i^* c_i}{\gamma_i^* m_i} = \rho_\circ \tag{A.14}$$

From A.14, the desired relations between γ_i^* and y_i^* are easily obtained:

$$y_i^* = \rho_\circ \frac{m_i}{c_i}\gamma_i^* \underset{\Uparrow\ eq.(A.11)}{=} \frac{\rho_\circ}{\rho}\left(1+\sum_{l=1}^{N_{solu}} m_l M_l\right)\gamma_i^* \tag{A.15}$$

or,

$$\gamma_i^* = \frac{1}{\rho_\circ}\frac{c_i}{m_i} y_i^* \underset{\Uparrow\ eq.(A.12)}{=} \frac{\rho - \sum_{l=1}^{N_{solu}} c_l M_l}{\rho_\circ}\gamma_i^* \tag{A.16}$$

A.4 Relations Between f_i^* and y_i^*

Using the same methodology as before:

$$\frac{\mu_i^{\bullet,x} - \mu_i^{\bullet,c}}{RT} = \ln\left(\frac{y_i^* c_i}{f_i^* x_i}\right) \tag{A.17}$$

The equations relating x_i and c_i, as given in Table 2.1, are:

$$\frac{x_i}{c_i} = \frac{\sum_{j=1}^{N_{spec}} x_j M_j}{\rho} \tag{A.18}$$

$$\frac{c_i}{x_i} = \sum_{l=1}^{N_{solu}} c_l + \frac{\rho - \sum_{l=1}^{N_{solu}} c_l M_l}{\sum_{m=1}^{N_{solv}} x_m' M_m} \tag{A.19}$$

Taking the limit, when $\sum_{l=1}^{N_{solu}} x_l \to 0$ or $\sum_{l=1}^{N_{solu}} c_l \to 0$, then $\frac{c_i}{x_i} \to \rho_\circ \Big/ \sum_{m=1}^{N_{solv}} x_m' M_m$. Applying it to equation A.17:

$$\frac{\mu_i^{\bullet,x} - \mu_i^{\bullet,c}}{RT} = \ln\left(\rho_\circ \Big/ \sum_{m=1}^{N_{solv}} x_m' M_m\right) \tag{A.20}$$

Comparing eqs. A.17 and A.20:

$$\frac{y_i^* c_i}{f_i^* x_i} = \frac{\rho_\circ}{\sum_{m=1}^{N_{solv}} x_m' M_m} \tag{A.21}$$

From A.21, the required relations between γ_i^* and y_i^* are the following:

$$y_i^* = \frac{\rho_\circ}{\sum_{m=1}^{N_{solv}} x_m' M_m} \frac{x_i}{c_i} f_i^* \underset{\text{eq.(A.18)}}{=} \frac{\rho_\circ}{\rho} \frac{\sum_{j=1}^{N_{spec}} x_j M_j}{\sum_{m=1}^{N_{solv}} x_m' M_m} f_i^* \tag{A.22}$$

or,

$$f_i^* = \frac{\sum_{m=1}^{N_{solv}} x_m' M_m}{\rho_\circ} \frac{c_i}{x_i} y_i^* \underset{\text{eq.(A.19)}}{=} \frac{\sum_{l=1}^{N_{solu}} c_l \sum_{m=1}^{N_{solv}} x_m' M_m + \rho - \sum_{l=1}^{N_{solu}} c_l M_l}{\rho_\circ} y_i^* \tag{A.23}$$

B. Density and Dielectric Constant for the Solvents

B.1 Introduction

In the following sections, the expressions used in this work to calculate the density and the dielectric constant of pure solvents, as a function of the temperature are given. These properties, like explained in chapter 4, are necessary to estimate the Pitzer-Debye-Hückel parameter $A_{DH,x}$. The capabilities of the Oster's mixing rule for predicting the dielectric constant of mixed solvents is also checked.

B.2 Density

The density ($\rho_m^\bullet$) of the solvents studied in this work, water, methanol and ethanol, are computed using the equation (DIPPR, 1984):

$$\rho_m^\bullet = A_1 / A_2^B \tag{B.1}$$

where the density is in $kmolm^{-3}$ and B is calculated by:

$$B = 1 + \left(1 - \frac{T}{A_3}\right)^{A_4} \tag{B.2}$$

and T is the absolute temperature in Kelvin.

The coefficients A_1, A_2, A_3 and A_4 are specific for each solvent. They were taken from DIPPR Tables (1984) and are presented in Table B.1.

Table B.1 Coefficients for pure solvent density calculation.

Solvent	A_1	A_2*10^1	A_3*10^{-2}	A_4*10^1
Water	4.6137	2.6214	6.4729	2.3072
Methanol	1.2057	1.9779	5.1263	1.7272
Ethanol	1.5223	2.6395	5.1625	2.3670

B.3 Dielectric Constant

The expression used to calculate the dielectric constant (ε_m) of a pure solvent m is (Maryott and Smith, 1951):

$$\log_{10}(\varepsilon_m) = C_1 + C_2(T - 273.15) \tag{B.3}$$

The coefficients C_1 and C_2, collected from Maryott and Smith (1951) for the solvents water, methanol and ethanol are presented in Table B.2.

Table B.2 Coefficients for the calculation of the solvent dielectric constant.

Solvent	C_1	C_2*10^3
Water	1.9460	-2.044
Methanol	1.5796	-2.640
Ethanol	1.4531	-2.700

B.4 Dielectric Constant of Mixed Solvents

Figure B.1 and Figure B.2 show that the Oster's mixing rule can describe correctly the dielectric constant for the mixed solvents water/methanol and water/ethanol. For both systems, the predictions are illustrated at two different temperatures, 298.15 K and 318.15 K.

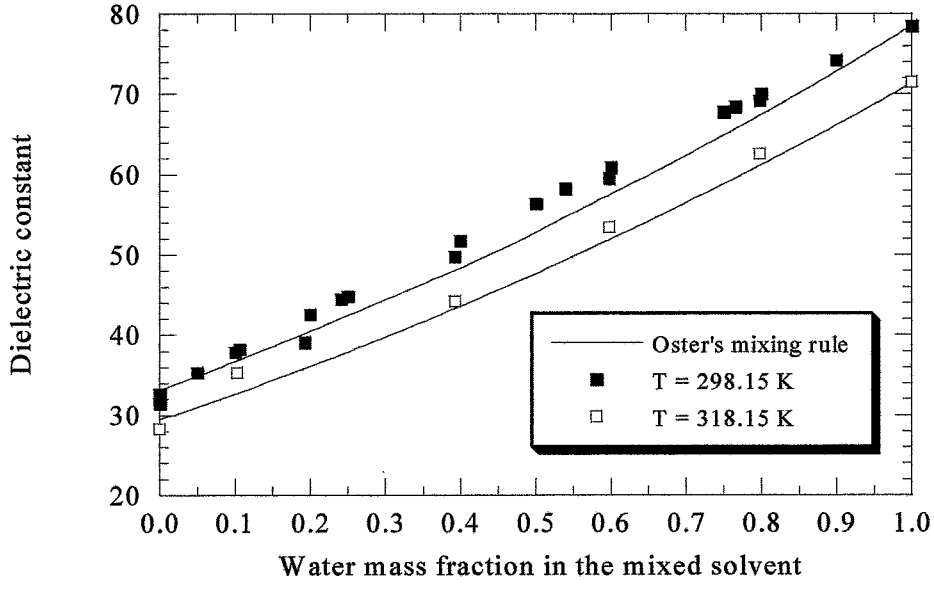


Figure B.1 *Comparison between experimental (Janz and Tomkins, 1972) and predicted curves with Oster's mixing rule, for the dielectric constant in the mixed solvent water/methanol.*

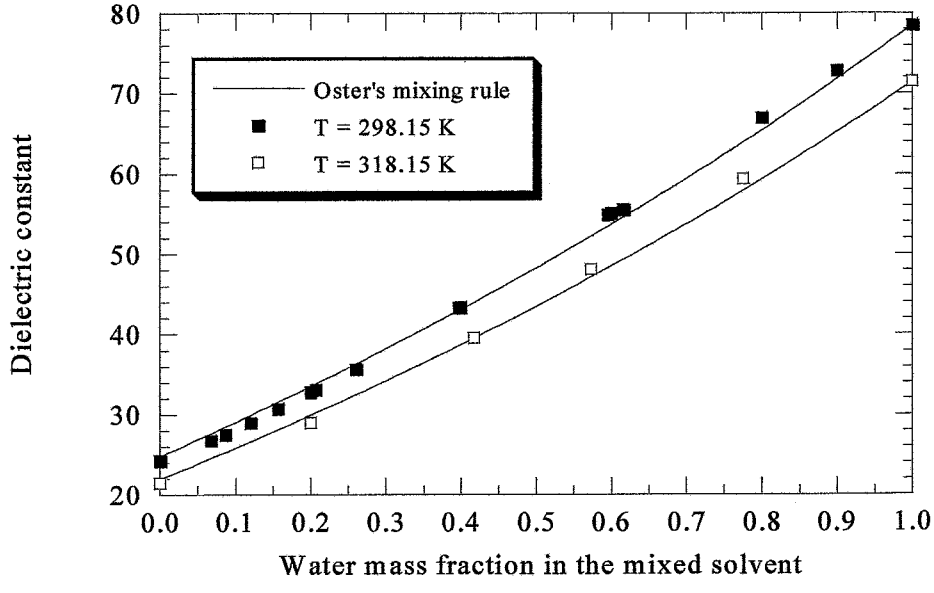


Figure B.2 *Comparison between experimental (Janz and Tomkins, 1972) and predicted curves with Oster's mixing rule, for the dielectric constant in the mixed solvent water/ethanol.*

C. Parameters for Weak Electrolytes Modelling

C.1 Introduction

In this appendix the expressions used to calculate the chemical equilibrium acid-base reactions constants of the amino acids and peptides in water, studied in chapter 5, the ionic product of water and the Debye-Hückel parameters are given. Those equilibrium constants, and the parameters for the Debye-Hückel equation, which depend on the temperature of the solution, were fitted to a second order polynomial on the temperature, according to the general expression:

$$Par = \alpha_0 + \alpha_1 T + \alpha_2 T^2 \qquad \text{(C.1)}$$

where Par means pK_1 or pK_2, which are the equilibrium constants in accordance with equations 5.3 and 5.4, or the Debye-Hückel parameters A or B. In equation C.1 α_0, α_1 and α_2 are the fitted parameters presented in the next section and T is the absolute temperature.

C.2 Chemical Equilibrium Constants

The parameters obtained for the representation of the amino acids equilibrium constants as a function of the temperature, using the data published by Izatt and Christensen (1973) and by King (1951), are listed in Table C.1.

Table C.1 Coefficients for the chemical equilibrium constants of the amino acids.*

Amino Acid	α_0	α_1*10^2	α_2*10^5
dl-Alanine	7.7018	-3.8881	5.3411
	28.345	-9.7007	11.750
Glycine	7.1157	-2.9548	4.5506
	26.155	-8.3834	9.6965
Hydroxyproline	7.2273	-3.4139	5.3636
	24.770	-7.8220	9.2390
dl-Isoleucine	6.9981	-3.0640	5.0129
	27.555	-9.2760	11.087
dl-Leucine	7.0040	-3.0337	4.9161
	27.433	-9.1848	10.910
dl-Norleucine	6.8528	-2.8962	4.6299
	27.405	-9.0778	10.681
Proline	7.3987	-3.5533	5.7879
	25.672	-7.5599	8.4482
Serine	7.6139	-3.3074	4.9864
	25.569	-8.4130	9.8118
dl-Valine	6.5886	-2.8617	4.7586
	26.936	-8.9094	10.514

*For each amino acid the first row is for pK_1 and the second for pK_2.

Since for peptides data is only available at 298.15 K (Izatt and Christensen, 1973), the corresponding equilibrium constants, are reported in Table C.2. This Table also gives the pK values for the amino acids for which no data was found for their temperature dependency or were only studied at 298.15 K.

Table C.2 *pK_1 and pK_2 values for some amino acids and peptides at 298.15 K.*

Substance	pK_1	pK_2
α-Amino n-butyric acid	2.291	9.832
α-Amino n-valeric acid	2.318	9.808
Threonine	2.090	9.100
Alanylalanine	3.120	8.296
Alanylglycine	3.160	8.240
Glycylalanine	3.170	8.230
Glycylglycine	3.060	8.130
Triglycine	3.260	7.910

For the ionic product of water (K_w), the following expression, proposed by Robinson and Stokes (1970), was applied:

$$pK_w = \frac{4471.33}{T} - 6.0846 + 0.017053T \qquad \text{(C.2)}$$

C.3 Parameters for the Debye-Hückel Equation

Robinson and Stokes (1970) compiled, for water, the values of the Debye-Hückel parameters at different temperatures. The expressions used in this work, were smoothed according to equation C.1. They are:

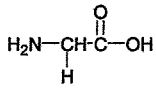
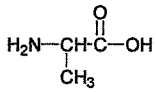
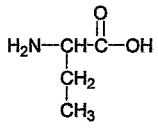
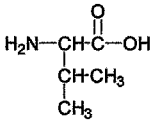
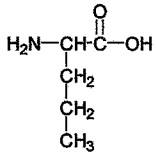
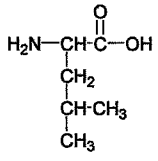
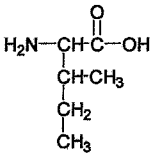
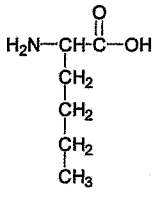
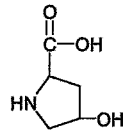
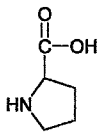
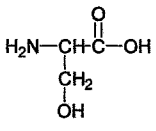
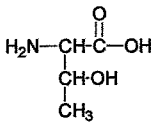
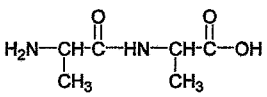
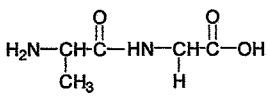
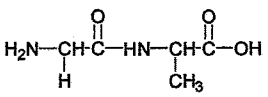
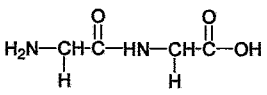
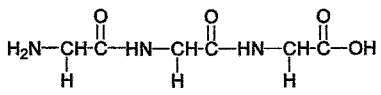
$$A = 1.6096 - 4.9865 * 10^{-3}T + 1.1863 * 10^{-5}T^2 \quad kg^{0.5}mol^{-0.5} \qquad \text{(C.3)}$$

$$B = 3.4974 * 10^{9} - 3.3349 * 10^{6}T + 8.8675 * 10^{3}T^2 \quad kg^{0.5}mol^{-0.5}m^{-1} \qquad \text{(C.4)}$$

D. Structures of the Amino Acids and Peptides

The structural formulas of the amino acids and peptides studied are given in Table D.1.

Table D.1 Structures of the studied amino acids and peptides.

 **Glycine**	 **Alanine**	 **α-Amino n-butyric acid**
 **Valine**	 **α-Amino n-valeric acid**	 **Leucine**
 **Isoleucine**	 **Norleucine**	 **Hydroxyproline**
 **Proline**	 **Serine**	 **Threonine**
 **Alanylalanine**	 **Alanylglycine**	 **Glycylalanine**
 **Glycylglycine**	 **Triglycine**	

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