Résumé

Différentes techniques de séparation sont en cours de développement dans les processus de purification des acides organiques pour faciliter leur passage de la phase non souhaitée à la phase souhaitée. L'extraction liquide-liquide est une méthode pertinente pour séparer les composants d'une phase à une autre. De nombreux travaux de recherche sont trouvés dans la littérature apparentés à l'étude de la récupération des acides organiques à partir des solutions aqueuses. L'objectif principal de ces études est d'avoir des données qui représentent le comportement de phases des mélanges contenant des acides organiques et de déterminer leur distribution entre phases à l'équilibre. Il ressort de ces études que l'efficacité d'un solvant organique dans les processus de l'extraction liquide-liquide des acides organiques à partir des solutions aqueuses est considérée comme l'un des critères pouvant influencer leurs distributions d'équilibres. Cependant, une détermination précise de l'équilibre de phases doit prendre en compte tous les critères pour juger de l'extraction d'un acide organique par un solvant. Il est révélé que la présence d'un électrolyte dans un mélange de solvants peut affecter le comportement de phases de ce mélange, et par conséquent les distributions des composants entre phases à l'équilibre peuvent subir des modifications importantes. Un acide faible est susceptible de se dissocier dans l'eau, d'où la nécessité de prendre cette considération en compte lors de la mise en place des méthodes basées sur des études expérimentales ou bien sur la modélisation thermodynamique de l'équilibre liquide-liquide.

Compte tenu de ce critère, l'aspect physico-chimique des acides organiques est pris en considération dans ce travail lors de la simulation de leur extraction à partir des solutions aqueuses en utilisant le processus liquide-liquide. L'effet des réactions chimiques qui se produisent dans la phase aqueuse sur le comportement des mélanges biphasiques est considéré dans le calcul de l'équilibre thermodynamique. Le présent travail porte sur la modélisation thermodynamique de l'équilibre liquide-liquide pour des systèmes ternaires et quaternaires et dont l'objectif est d'apporter une nouvelle contribution à la modélisation des phases liquides en considérant la présence d'espèces chargées issues de la dissociation des acides organiques. La modélisation d'équilibres entre phases est menée en s'appuyant sur des données expérimentales disponibles dans la littérature afin de prédire le comportement de phases des mélanges ternaires et quaternaires. Les calculs d'équilibres liquide-liquide sont accomplis en appliquant le modèle UNIQUAC-Électrolyte. Les paramètres du modèle utilisé dans ce travail sont ajustés en décomposant les mélanges principaux en sous-mélanges binaires. Cette démarche de calcul est utilisée pour prédire les compositions d'équilibres ternaires et quaternaires dans la phase aqueuse et dans la phase organique en présence des électrolytes. Les champs de validité des résultats issus de la modélisation en tenant compte la dissociation des acides organiques dans leurs milieux aqueux sont justifiés par comparaison avec des résultats expérimentaux issus de la littérature où aucune dissociation n'a été considérée. Pour voir l'effet de cette considération sur des mélanges biphasiques, les comportements de phases obtenus par des données issues de la modélisation sont comparés au ceux de la littérature. Les résultats montrent que les données d'équilibres issues de la modélisation sont déviées par rapport à celles tirées de différentes sources.

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Study and Thermodynamic Modeling of Phase Equilibrium for Aqueous-Organic Electrolyte Two-Phase Systems

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Study and Thermodynamic Modeling of Phase Equilibrium for Aqueous-Organic Electrolyte Two-Phase Systems

Soutenue le Jeudi 05 novembre 2020 à 10h00 devant la commission d'examen :

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Study and Thermodynamic Modeling of Phase Equilibrium for Aqueous-Organic Electrolyte Two-Phase Systems

General Introduction

Among the most separation techniques extensively used in chemical process industries, the liquid-liquid extraction is a relevant method for separating components from one phase to another. The research field related to the separation of components from various types of mixtures using the liquid-liquid separation technique was aroused and is still attracting an ever-increasing interest. The investigation of liquid-liquid equilibrium for multicomponent systems is of practical importance to obtain data representing their phase behavior. Furthermore, knowledge of liquid-liquid equilibrium for multicomponent electrolyte systems presents a crucial advantage in evaluating the effect of electrolytes on the liquid-liquid separation process.

The objective of this work was focused on the thermodynamic modeling of liquid-liquid equilibrium for ternary and quaternary systems. The purpose of the work was to present a thermodynamic treatment different to that available in the literature concerning the separation of organic acids from aqueous solutions. This has been done assuming a partial dissociation of organic acids in aqueous solutions and extending this consideration to aqueous-organic mixtures. It would be necessary for a thermodynamic modeling framework of multicomponent liquid-liquid equilibrium for mixtures involving electrolytes to use different types of data. To predict the phase behavior of ternary and quaternary mixtures, and depending on the availability of data in the literature for binary submixtures, phase equilibrium modeling for two-phase mixtures was carried out. The Extended UNIQUAC model was used to model binary vapor-liquid equilibrium as well as binary, ternary and quaternary liquid-liquid equilibrium to predict phase equilibrium data for ternary and quaternary mixtures. Electrolytes resulting from the first dissociation equilibrium of organic acids in aqueous solutions were considered in the modeling process of phase equilibrium for ternary and quaternary mixtures to evaluate the performance of the Extended UNIQUAC model in predicting ternary and quaternary equilibrium compositions between two liquid phases from binary data and analyze the effect of this consideration on the phase behavior of mixtures compared to the existing description in the literature for the same mixtures where no partial dissociation of organic acids was considered. Phase diagram representations of aqueous-organic two-phase mixtures included organic acids available in the literature were performed in the absence of ionic species and only the undissociated forms in aqueous solutions were considered. The presence of ionic species can mainly affect the distribution of components between liquid phases so that the application of a new method for describing the phase behavior of two-phase mixtures involved both undissociated and dissociated forms of organic acids in the aqueous phase represents in some way a separation process of practical interest based on the liquid-liquid equilibrium.

The first Chapter of this thesis focuses on the separation of organic acids from aqueous solutions by liquid-liquid extraction. This includes the identification of general concepts and the methods by which the separation of organic acids from aqueous solutions can be evaluated. This Chapter presents the importance of considering aqueous speciation in the liquid-liquid separation technique. The motivations and objectives of the thesis are given at the end of this Chapter. The second Chapter deals with the thermodynamics of electrolytes related to the workspace of this thesis. A literature survey on some electrolyte thermodynamic models is also presented in Chapter 2. The third Chapter highlights the calculation procedure used in the correlation and prediction of thermodynamic properties. The fourth and fifth Chapters present the core of this thesis on phase equilibrium modeling of ternary and quaternary two-phase mixtures including electrolytes. The results obtained are also given in these Chapters. The sixth Chapter presents the thermodynamic modeling of vapor-liquid equilibrium for binary systems.

Introduction Générale

Parmi les techniques de séparation les plus utilisées dans les procédés industriels des industries chimiques, l'extraction liquide-liquide est une méthode pertinente pour séparer les composants d'une phase à l'autre. La séparation des composants des mélanges de différents types en utilisant la technique de séparation liquide-liquide a attirée et suscite toujours un intérêt croissant dans les travaux de recherche liés à ce domaine. L'étude de l'équilibre liquide-liquide pour des systèmes multicomposants permettant d'avoir des données qui représentent leur comportement de phases constitue une importance pour les procédés de séparation. De plus, la connaissance de l'équilibre liquide-liquide pour des systèmes à plusieurs composants contenant des électrolytes présente un avantage crucial dans l'évaluation de l'effet des électrolytes sur le processus de séparation liquide-liquide.

L'objectif de ce travail était basé sur la modélisation thermodynamique de l'équilibre liquide-liquide pour des systèmes ternaires et quaternaires. Le but de ce travail est d'apporter une contribution en présentant un traitement thermodynamique différent de celui disponible dans la littérature concernant la séparation des acides organiques à partir de leurs solutions aqueuses. Pour cela, il a été supposé qu'une dissociation partielle des acides organiques a eu lieu au sein de leurs solutions aqueuses et en étendant cette considération aux mélanges des deux phases liquides aqueuse et organique. Il serait nécessaire d'utiliser différents types de données dans un cadre de modélisation thermodynamique de l'équilibre liquide-liquide pour des mélanges à plusieurs composants impliquant des électrolytes. Pour prédire le comportement de phases des mélanges ternaires et quaternaires, et en fonction de la disponibilité des données pour des sous-mélanges binaires dans la littérature, une modélisation d'équilibre entre phases pour des mélanges biphasiques a été réalisée. Le modèle UNIQUAC-Électrolyte a été utilisé pour modéliser l'équilibre vapeur-liquide des mélanges binaires ainsi que l'équilibre liquide-liquide des mélanges binaires, ternaires et quaternaires afin de prédire les données d'équilibre de phases pour des mélanges ternaires et quaternaires. Les électrolytes résultant d'équilibre de la première dissociation des acides organiques dans les solutions aqueuses ont été considérés dans le processus de la modélisation de l'équilibre de phases pour des mélanges ternaires et quaternaires afin d'évaluer les performances du modèle UNIQUAC-Électrolyte dans la prédiction des compositions d'équilibre entre deux phases liquides pour des mélanges ternaires et quaternaires à partir de données binaires et analyser l'effet de cette considération sur le comportement de phases des mélanges par rapport à la description existante dans la littérature pour les mêmes mélanges où aucune dissociation partielle des acides organiques n'a été envisagée. Les représentations des diagrammes de phases des mélanges à deux phases liquides aqueuse et organique comprenant des acides organiques disponibles dans la littérature ont été obtenues en l'absence des espèces ioniques et seules les formes non dissociées dans des solutions aqueuses ont été prises en compte. La présence des espèces ioniques peut affecter principalement la distribution des composants entre les phases liquides alors que l'application d'une nouvelle méthode pour décrire le comportement de phases des mélanges biphasiques impliquant des formes non dissociées et dissociées d'acides organiques dans la phase aqueuse représente en quelque sorte un processus de séparation d'intérêt pratique basé sur l'équilibre liquide-liquide.

Le premier Chapitre de cette thèse porte sur la séparation des acides organiques à partir des solutions aqueuses par l’extraction liquide-liquide. Cela comprend l'identification de concepts généraux et les méthodes par lesquelles la séparation des acides organiques à partir des solutions aqueuses peut être évaluée. Ce Chapitre présente l’importance de considérer la spéciation aqueuse dans la technique de séparation liquide-liquide. Les motivations et les incitations de la thèse sont données à la fin de ce Chapitre. Le deuxième Chapitre traite la thermodynamique des solutions d’électrolytes liée au champ de travail de cette thèse. Une revue bibliographique sur certains modèles thermodynamiques des solutions d’électrolytes est également présentée au Chapitre 2. Le troisième Chapitre met en évidence la procédure de calcul utilisée dans la corrélation et la prédiction des propriétés thermodynamiques. Le quatrième et le cinquième Chapitres présentent l’essence de cette thèse consacrée à la modélisation de l'équilibre de phases des mélanges ternaires et quaternaires à deux phases liquides contenant des électrolytes. Les résultats obtenus sont également donnés dans ces Chapitres. Le sixième Chapitre présente la modélisation thermodynamique de l'équilibre vapeur-liquide des systèmes binaires.

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Nomenclature

A	Debye-Hückel parameter
a_w	Activity of water
F	Flow rate of the feed
f_i	Fugacity of component (i)
f_i°	Fugacity of component (i) in the standard state
G	Gibbs free energy of a solution
G^{id}	Gibbs free energy of an ideal solution
G^E	Excess Gibbs energy
H	Henrys law constant
I	Ionic strength
K_i	Distribution coefficient of component (i)
L^{aq}	Flow rate of the aqueous phase
L^{org}	Flow rate of the organic phase
M_w	Molecular weight of water
m_i	Molality of species (i)
N	Number of components
Ndata	Number of tie lines
P	Pressure
q_i	Surface area parameter of component (i)
R	Gas constant
r_i	Volume area parameter of component (i)
S	Selectivity
T	Absolute temperature
x_i^{org}	Composition in the organic phase of component (i)
x_i^{aq}	Composition in the aqueous phase of component (i)
x_i	Mole fraction of component (i) in the liquid phase
$x_{CA\pm}$	Mean ionic mole fraction
y_i	Mole fraction of component (i) in the vapor phase
Z	Coordination number
z_i	Charge of ion (i)

Greek symbol

φ_i	Volume area fraction of component (i)
θ_i	Surface area fraction of component (i)
Δu_{ji}	Binary interaction parameters
Ψ_{ji}	Interaction parameter

γ^{∞}	Unsymmetrical activity coefficient
γ	Symmetrical activity coefficient
γ_i^{D-H}	Debye-Hückel contribution to the activity coefficient of an ionic species (i)
γ_w^{D-H}	Debye-Hückel contribution to the activity coefficient of water
γ_i^{Com}	Combinatorial contribution to the activity coefficient of component (i)
γ_i^{Res}	Residual contribution to the activity coefficient of component (i)
$\gamma_{CA\pm}$	Mean ionic activity coefficient
φ	Osmotic coefficient
υ	Stoichiometric coefficient
μ_i	Chemical potential of component (i)
μ°_i	Chemical potential of component (i) in the standard state
φ_j^V	Fugacity coefficient of component (j) in the vapor phase
φ_j^s	Fugacity coefficient of pure component (j) in its saturated state

Abbreviations

ARD	Absolute relative deviation
LLE	Liquid-liquid equilibrium
MAD	Mean absolute deviation
RMSD	Root mean square deviation
UNIQUAC	Universal Quasi-Chemical
VLE	Vapor-liquid equilibrium

Superscripts

cal	Calculated value
exp	Experimental value
aq	Aqueous phase
org	Organic phase
Com	Combinatorial term
Res	Residual term
D - H	Debye-Hückel term

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1. Literature review and thesis background

1.1 Introduction

Different separation techniques are being developed in the purification processes to obtain organic acids that satisfy closely the needs of different customers requiring the highest purity of the final product. Due to their importance in various industrial applications, the purification of organic acids becomes the primary challenge to snatch them from mixtures.

The different aspects of mixtures behavior constitute challenges which require a comprehensive survey including the choice of separation techniques, the number of phases at equilibrium and the distribution of components between phases. The success or failure of a separation method does not only depend on its ability to isolate the desired components and facilitate their move from the unwanted phase to the wanted phase. Alternatively, regardless of the separation method used, the nature of a mixture should be considered in the separation processes to ensure efficient mass transfer between phases truly representative of interest.

Distillation, extraction, crystallization, and others are the most separation methods widely applied in chemical engineering to recover organic acids from aqueous solutions. The common point of these separation techniques is based on the recovery of the desired components from the unwanted ones. This is accomplished by transferring one or more components between phases depending on the type of separation techniques used and on the nature of mixtures.

The separation of constituents of a mixture depends essentially on the physicochemical aspects of these constituents. The identification of the physical and chemical properties of mixture components allows using the appropriate separation method. From a practical point of view, the effectiveness of separation techniques for selecting one component or more from the others relies mainly on differences in the physical or chemical properties of components. The appropriate technique for separating components consists of applying a specific method adapted to the nature of mixture components to recover the desired products effectively. Among different separation techniques applied to mixtures in engineering applications associated with chemical process industries, the most mixtures commonly encountered restricted to:

Separation of petroleum refining, petrochemical and natural gas products by using distillation to separate one or more light components from the heavy ones contained in a mixture;

Separation of pharmaceutical and fine chemical products by using crystallization, this separation process is classified into three types that can be applied depending on the properties of systems and necessarily on the properties of compounds to be crystallized. Evaporation, cooling and precipitation are frequently the types of crystallization used in chemical process industries;

Separation of biological and environmental products and other applications in the industry use the filtration. Depending on the nature of mixtures between solid and liquid phases, vacuum, cold, hot and others are the main types of filtration;

Pharmaceutical and environmental products can be separated by using the liquid-liquid extraction process. The field of this application covers the chemical, metallurgical, petrochemical industries. The purpose of the liquid-liquid extraction process is to separate or remove one or more desired products from a mixture initially containing two or more miscible liquids by adding a third liquid. Generally, the separation is accomplished by using a solvent which is preferentially miscible with one of them.

Solvent extraction or liquid-liquid separation of two liquid phases is a technique used to separate components based on a difference in their solubilities in different solvents. The phases may be immiscible or partially miscible liquids. The principle of the liquid-liquid extraction is to conduct the process correctly i.e. a solvent must be added to a mixture of miscible liquids creating two liquid phases. The effectiveness of a solvent that causes a heterogeneous mixture splitting an initial feed solution into two liquid phases is then tested by its selectivity to take off one component from the other.

Distillation and extraction are two types of separation widely used in chemical industries. The former is commonly used to separate miscible liquid mixtures by taking the relative volatility of components as a criterion of distillation efficiency, the one with the highest relative volatility ascends to the top of the column while the heaviest flows at the bottom of the column. While distillation processes rely on an intimate contact of the liquid and vapor phases until a state of equilibrium is achieved, the liquid-liquid extraction is based on the same principle i.e. an intimate contact takes place between two liquid phases. The solvent extraction process is promoted by solvent molecules present in a mixture whose solubility determines the separation power.

Recovery of an organic acid from an aqueous solution is commonly carried out by introducing an organic solvent into the mother solution. The amounts of a solvent that can be added in series in separation sequences depend both on the compositions of components present in the aqueous solution and the appearance of heterogeneous mixtures. Further, the liquid mixtures must be thoroughly mixed to facilitate mass transfer between liquid phases. The process of liquid-liquid extraction is based on the mass transfer of a solute from one phase to another.

Organic solvents are added to an aqueous solution to attract organic components contained in this solution by holding more or less depending on the differences in chemical properties between a diluent and an organic solvent. Indeed, the transfer of a solute depends on the nature of the solvent molecules present in a mixture. The immiscibility between water and an organic solvent creates an irregular distribution of a solute between liquid phases. As a result, the feed solution may lose a significant part of its mass. Consequently, the solute molecules enrich the organic phase then, a state of equilibrium can exist between liquid phases. To ensure equilibrium between phases, intimate contact of liquid mixtures with agitation for a sufficient period of time is required to guarantee a complete mass transfer of components between phases and to enrich the organic phase with organic components.

The solution is characterized by two main areas, a heavy liquid identifies the aqueous solution which contains water molecules and a part of the solute concentration, and a light liquid identifies the organic phase which contains the organic solvent molecules and a part of the solute concentration. The compositions of the mixture components in the two liquid phases are then analyzed by different methods. Graphically, liquid-liquid extraction is represented by an equilateral triangular phase diagram which represents the mass fractions or the mole fractions of components of a ternary or even a quaternary system. Each component of a system at its purity of one hundred percent is represented at each corner of the triangle and the compositions of components distributed between the liquid phases are represented by tie lines.

1.2 General notions of liquid-liquid equilibrium

The demand for applying improved methods of purification or recovery of organic acids has expanded over the past years. Due to their use in many industrial applications [1-4] important attempts have been carried out to test various techniques for extracting organic acids from the aqueous phase to the organic phase [5-11].

Due to its use in a wide range of applications in chemical engineering, liquid-liquid extraction plays an important role in the separation processes. Among all separation techniques, the main features of liquid-liquid extraction differ from those of other methods. The characteristics of liquid-liquid extraction have had and continue to have a significant effect on separation processes by offering many benefits such: simple, effective, less expensive and controllable conditions.

Generally, an organic acid has a high affinity with water in aqueous solution and its recovery from this phase to another needs a third component that must be added to create a movement of solute molecules. Indeed, the process of removing an organic acid from an aqueous solution involves adding at least one solvent to that solution. It was found that organic solvents can be used to dissolve a large portion of a solute and they have a great power to transfer a solute from the unwanted phase to the wanted phase. [12] The application of organic solvents in the design of separation processes facilitating the recovery of organic components from an unwanted phase becomes a strategy of interest for research laboratories.

Distribution coefficient

Regardless of the effectiveness of a solvent, the solvent extraction process enables to establish both chemical and physical activities of a solute in a created phase. Such a phase would be necessarily different from the feed phase. Indeed, after vigorous and steady agitation followed by decantation, a concentration would emerge in the solvent phase. Somehow, this concentration would diminish the initial concentration initially existed in the aqueous solution with complete solubility in water. The compositions of an organic acid in the liquid phases are defined by the so-called distribution coefficient.

The liquid-liquid extraction process generally occurs when two components are placed into contact with each other leading to create two immiscible liquid phases. This condition is a prerequisite to be considered for better controlling solvent extraction processes. Mutual solubility between two liquid components is an essential factor to separate components that exist initially in one of the two liquids

Based on their solubility in the two immiscible liquids, components are separated into two portions in the solvent extraction technique. The most important point in the partition of a solute between two liquid phases presents an important concept based on the distribution coefficient between inorganic and organic phases. Separation by recovering organic compounds from aqueous solutions using solvent extraction is a relevant technique that depends on the unequal distribution of a solute between two liquids, practically immiscible [13-14]. The ability of a solvent in extracting dissolved components from the aqueous layer to its layer is evaluated through the solute distribution between phases [12]. The distribution coefficient distinguishes the effect of one solvent compared to another one in transferring a solute and allows quantifying the mass transfer of a solute between phases. In other words, this relies on the amount of solvent needed by which the solute compositions of coexisting phases at equilibrium are established. The solute distribution coefficient between two liquid phases is defined as the ratio of the composition of a solute (i) in the solvent phase (org) to that of a solute (i) in the aqueous phase (aq)[12]:

$$K_i = \frac{x_i^{org}}{x_i^{aq}} \qquad \textbf{(1-1)}$$

K_i, x_i^{org}, x_i^{aq} are the solute distribution coefficient and the compositions in the organic and aqueous phases of a solute (i), respectively.

Selectivity

The liquid-liquid extraction process may be facilitated by the presence of components capable of attracting solute molecules from one phase to another. This means that a solute will be transferred from the aqueous phase to the organic phase if its solubility in an organic solvent is high comparable to that in water. In other words, the solvent which would minimize its losses in the aqueous solution would adequately select solute molecules and snatch them from the aqueous solution [15]. A parameter for measuring the affinity of a solute toward a solvent is defined by the selectivity. When a mixture contains more than one solute, the selectivity of a solvent takes advantage to extract a desired component from the feed solution. The selectivity of a solvent for a solute (i) from solute(i)-component(j) mixture is expressed as follows [12]:

$$S = \frac{K_j}{K_i} \tag{1-2}$$

S, K_j, and K_i are the selectivity and the distribution coefficients of components (j) and (i), respectively.

Information about the distribution coefficient, extraction power of a solvent, mutual solubility between liquids, etc, require knowledge of properties, in particular, thermodynamic properties of components of mixtures. In order to distinguish the degree of separation of mixtures containing organic components while the liquid-liquid extraction process is used to recover such components, these concepts should be used to evaluate and test various types of organic solvents. Moreover, the description of the liquid-liquid extraction process relies on the separation yield of components by determining the phase equilibrium of mixtures.

The determination of the compositions of coexisting phases at equilibrium is an essential element in the study of separation processes. The liquid-liquid extraction process is involved in separating various types of mixtures of considerable interest in chemical processes. Such processes need to be described for design and optimization purposes. The separation characteristics of components from liquid mixtures by using the liquid-liquid extraction process rely on using different methods to evaluate phase equilibrium data.

1.3 Literature review

1.3.1 Experimental framework in studying liquid-liquid equilibrium

In the last decades, research activities devoted to the separation of organic acids from aqueous solutions through the liquid-liquid extraction process have been expanded. Several research works have been carried out by studying different systems containing water, organic acids and organic solvents. Various types of organic solvents have been examined to test their influence in improving the recovery of organic acids from aqueous solutions. The study of liquid-liquid equilibrium for ternary and quaternary mixtures containing commonly different organic acids has been evoked by a large number of works aimed to ascertain and compare the phase behavior and the equilibrium data of various types of mixtures.

Determination of binodal and tie line data

A significant part related to the topic of the separation of organic acids was based on an experimental framework. Concentrated attention has been given in the literature to the study of the purification of organic acids by carrying out experimental measurements. This is based on a description of the experimental apparatus and the materials used in the extraction process. Temperature and pressure conditions are specified throughout the experimental process. The binodal curve of mixtures is determined by the cloud point method. Such a method relies on preparing a series of binary mixtures containing water+a solute and an organic solvent+a solute of known compositions. The third component that tends to bring a mixture from homogeneous to heterogeneous behavior is vigorously added. The components of a mixture are brought into contact with each other to check for any phase splitting. If this happens, the two phases begin to appear. In order to measure the liquid-liquid equilibrium tie line data, mixtures of known compositions containing water+a solute+an organic solvent are prepared. Then, the mixture is vigorously shaken over a period of time to achieve a complete mass transfer and ensure a state of equilibrium. After that, the mixture would split into two layers; one at the top represents the organic phase and the other at the bottom represents the aqueous phase.

A description of the properties of systems can be achieved either by performing an experimental analysis of samples or by calculating mass balances. Then, the determined measurements of the mutual solubility data between an organic solvent and water, phase equilibrium data and organic acid distribution coefficients between phases are outlined. The role of experimental data remains important for linking these experimental analyzes to theoretical relationships. Furthermore, experimental data are useful for specifying the properties of mixtures by determining the equilibrium compositions of components in general, and for organic acids in particular, and for verifying the effectiveness of products used in separating components.

It is anticipated that an experimental framework for any separation process will be more advantageous and can be used to optimize and improve the separation of components. Emphasize that experimental measurements are needed to collect specific data that can only be obtained through experimental measurements. Indeed, the collection of experimental measurements, if the operating conditions allow conducting an experimental study, is commonly apprehended. Industrial processes require research studies relating to the liquid-liquid equilibrium of the mixtures involved and are of great importance for the realization, analysis and interpretation of the phase diagram of mixtures. The knowledge of the phase diagram of a mixture refers to the determination of the thermodynamic properties of multicomponent mixture. Like any separation technique, the liquid-liquid equilibrium method requires a description of the phase diagram which presents phase equilibrium properties of mixtures.

A description based on experimental measurements of liquid-liquid equilibrium is essential for the processing and following up phase diagrams of mixtures. They enable to study the state of mixtures by varying both chemical and physical conditions leading to the formation of liquid phases. Information about the phase behavior of mixtures whose separations are based on the liquid-liquid equilibrium technique can be obtained by performing experimental measurements. However, experimental data are not always available and would not be extended to include all mixtures under all operating conditions. Depending on the availability of experimental liquid-liquid equilibrium data in some cases or absence in some others, a theoretical framework is required. A complete description of understanding the basic concepts related to the liquid-liquid equilibrium technique needs theoretical methods. Thermodynamics of mixtures provide a way to treat the phase behavior of immiscible liquids by using reliable methods for the identification of liquid phase compositions. The principle relies on the formulation of mathematical models to determine the thermodynamic properties of mixtures under specific conditions. Furthermore, mathematical models give a specific way to determine and test the phase behavior of a mixture in comparison with experimental measurements. Mathematical models can have a significant effect on the evaluation of experimental measurements and the consistency of data produced by a mathematical model can be checked by referring to the available experimental data.

It is unlikely that high design tendencies related to the separation of organic acids through the liquid-liquid equilibrium technique can only be reached by carrying out experimental measurements under specific conditions. In contrast, a mathematical model would never be developed to give an appropriate description of the phase behavior of a mixture without recalling accurate experimental measurements. The study of the phase behavior between liquid phases can be performed using experimental measurements, mathematical models or both to check the reliability and adequacy of thermodynamic properties. It is interesting to note that most mathematical models treating the thermodynamics of mixtures are generated using some experimental information. This means that the development of a mathematical model needs a minimum of experimental information about all submixtures constituting the main mixture to calculate its thermodynamic properties. This requires improvement and availability of experimental data for different types of mixtures, which is not generally the case, especially for mixtures with complex phase behavior. In this context, enhancing the accuracy of a thermodynamic model can be achieved by exploiting the available experimental data. The ability of a thermodynamic model can be tested to represent a phase behavior outside the available experimental data, which have already been used to verify its capacity in representing such data.

1.3.2 Theoretical framework in studying liquid-liquid equilibrium

The study of separation problems related to the purification of organic acids demands the application of different techniques. Further to the experimental aspect that would identify the thermodynamic characteristics of mixtures involved organic acids, a theoretical aspect based on the application of the concepts of the thermodynamics of mixtures is needed to determine the mass transfer of solutes between immiscible liquids and interpret the phase behavior depicted using experimental data.

The liquid-liquid equilibrium processes may recognize a phase change needing deep analysis and systematic treatment to optimize such processes. Various situations can influence the equilibrium between liquid phases. Indeed, a theoretical background based on a mathematical formulation must be applied to solvent extraction processes to understand the phase behavior and control the thermodynamic properties of mixtures by evaluating various parameters i.e. temperature, pressure and their effect on the equilibrium data of the two liquid phases. The procedure relies on phase equilibrium calculations of liquid mixtures through applying functions that depend on specific properties of such mixtures.

As pointed out previously, the adoption of different ways for obtaining useful information about liquid-liquid separation properties and checking the inadequacies of the distribution coefficient of components shared between two partially miscible or immiscible liquids is very important. The knowledge of these descriptions using thermodynamic functions is a useful way to simulate the process of separating components from liquid mixtures by identifying the conditions leading to a state of thermodynamic equilibrium and determining the liquid phase compositions. Such compositions refer to phase compositions of aqueous-organic two-phase systems at equilibrium at a given temperature and pressure. These data need to be identified for each mixture when a separation of type liquid-liquid equilibrium process is applied. At this point, the investigation of the phase equilibrium diagrams between liquid phases lies in applying theoretical concepts based on computational procedures to obtain a phase diagram representing the behavior of mixtures involved organic acids. Finding the distribution of organic acids between two partially miscible or immiscible liquids needs feasible strategies by using useful tools of thermodynamics.

Thermodynamic characteristics of the state of mixtures whose separation processes are carried out via the liquid-liquid equilibrium technique are based on the theoretical aspects of thermodynamics represented by mathematical terms. Combining a thermodynamic treatment with a mathematical formulation has been elaborated to represent the phase behavior of mixtures. The separation of mixture components through the liquid-liquid equilibrium technique has become prevalent. Particular attention has been paid to the development of methods to simulate the process of recovery of organic acids from aqueous solutions. As a result, several research works have been treated the process of recovery of organic acids from aqueous solutions by using both theoretical and experimental frameworks in most cases, and in others, a theoretical context is used to treat that process with limited experimental data. The purpose of these methods is to calculate the liquid-liquid equilibrium data for ternary and quaternary systems containing water, organic acids and organic solvents. Different calculation methods with different approaches were applied to obtain a representation of phase diagrams of ternary and quaternary systems containing organic acids. In most cases, phase diagram representation of calculated liquid-liquid equilibrium data was compared with that of experimental liquid-liquid equilibrium data to test the efficiency and reliability of the methods used in calculating equilibrium data between aqueous and organic phases. Such methods were used to describe the phase equilibrium between liquid phases by applying equations based on the thermodynamics of mixtures.

Methods for phase equilibrium modeling

The resolution of the phase equilibrium of the liquid-liquid equilibrium process relies on the application of thermodynamic principles to determine quantities between two coexisting phases. This was carried out by using thermodynamic models to identify the compositions of aqueous and organic phases at equilibrium. In general, flash calculations of phase equilibrium properties have been widely performed by attributing two main methods. The most common is based on the activity coefficient models (ACM) (excess Gibbs energy models) i.e. NRTL, WILSON, UNIQUAC, UNIFAC, and the second is depended on the equations of state (EoS) i.e. REDLICH-KWONG (RK), SOAVE-REDLICH- KWONG (SRK) and PENG-ROBINSON (PR). Compared to the first method, equations of state (EoS) are less recommended in the calculation of phase equilibrium data of two liquid phases because their pronounced meaningful effect can be beneficial for vapor-liquid equilibrium mixtures at high pressures [16]. At low pressures, activity coefficient models can be used to represent liquid and vapor phases. The calculation of thermodynamic properties and the distribution of components between phases using thermodynamic models have received great attention. Numerous works available in the literature have been devoted to the application of different activity coefficient models to describe the phase equilibrium of mixtures containing organic acids. Identification and description of the equilibrium between two liquid phases are essential for the design of liquid-liquid equilibrium process. The nature of a mixture needs to be considered in a description of its behavior. This can be done by using a suitable thermodynamic model to simulate a separation process based on the calculation of thermodynamic properties between phases.

The simulation of the process of separating organic acids from aqueous solution was conducted using the excess Gibbs energy models. In principle, and for most excess Gibbs energy models, the calculation of liquid-liquid equilibrium data requires the adjustment of parameters. In other words, a description of the phase behavior of a mixture related to obtaining phase equilibrium data through using activity coefficient models needs to assign optimal values to these parameters. In excess Gibbs energy models, interaction forces between two or more components of a mixture are assigned to be assembled, one with each other, according to parameters. These parameters correspond to the interactions engendered between different components of a mixture. Each pair of components of a mixture is often represented by two parameters. In some cases, the regression of these parameters was made using some experimental data depending on the type of different submixtures constituting the main mixture, and in other cases, optimal parameters were obtained by regression of the unknown parameters to ternary or quaternary experimental liquid-liquid equilibrium data. In both cases, numerical methods were used to estimate these parameters. The implementation procedure implies attributing thermodynamic equilibrium conditions for phases that coexist in equilibrium. The computational approach for obtaining equilibrium data is based on the resolution of a set of equations satisfying the equilibrium conditions. This criterion was commonly adopted to search for realistic data. In the case of two-phase systems, phase equilibrium data between the aqueous and organic phases of mixtures containing organic acids were determined through defining equilibrium criteria for each component two-phase systems. The reliability of the calculated liquid-liquid equilibrium data was compared with the experimental data. The deviations between the calculated and experimental equilibrium properties of aqueous-organic phases were determined to check the accuracy of the model used.

1.3.3 Thermodynamics of the liquid-liquid equilibrium

While it appears from a literature survey, the separation of organic acids from aqueous solutions has been raised different issues that would in some way affect the transition of an organic acid from unwanted phase to wanted phase. In this context, the distribution of organic acids between the aqueous and organic phases has been considered to be a criterion of success or failure of a solvent extraction process. It depends heavily on their solubility in either of the solvents [12]. Besides the distribution of organic acids between two liquid phases, limited liquid miscibility is considered to have a significant effect on the solvent extraction process [17]. While the effect of pressure is assumed to be neglected, the temperature effect would affect the liquid-liquid equilibrium [18].

Types of liquid-liquid systems

The extraction of an organic acid from an aqueous solution occurs when it disperses between partially miscible or immiscible solvents, and the presence of two liquid phases can be checked either experimentally or by calculation. Moreover, there are two common types of ternary liquid-liquid systems. They can be distinguished either by one or two partially miscible binaries. When mutual solubility data are available for partially miscible binaries, and parameters are known for the third completely miscible binary, there would be no difficulties encountered in determining the phase behavior for the second type [19]. In the first type of ternary liquid-liquid system, a critical point where the compositions of the two liquid phases are identical, and beyond that point, the limit of the coexistence of liquid phases reaches the end. The plait point is located somewhere in the top region whose name is the binodal curve

[20]. The binodal curve distinguishes the mutual solubility between two components involved in a ternary system.

However, using only binary data can raise difficulties in describing a phase diagram for the first type. Such a type is characterized by two completely miscible binaries and one partially miscible pair. Following this scheme, binary parameters of an activity coefficient model are determined using mutual solubility data for the partially miscible pair and vapor-liquid equilibrium data for the completely miscible binaries [19]. While typical experimental vapor-liquid equilibrium data are often not available, it is very difficult to use such data to adjust interaction parameters for the completely miscible subsystems, and therefore many sets of binary parameters would be established for a fixed binary system [19]. Under these conditions, and since experimental vapor-liquid equilibrium data are often not available for binary mixtures with specific properties, it is unlikely probable to calculate ternary liquid-liquid equilibrium data using only binary data [20]. In this context, and by using only binary data, the description of multicomponent liquid-liquid equilibrium would be more difficult than that of multicomponent vapor-liquid equilibrium. However, the best sets of binary parameters are those whose representation of vapor-liquid equilibrium is the best [19]. In addition, it is possible to obtain reliable liquid-liquid equilibrium data for ternary systems with a plait point using just binary data provided to use accurate excess Gibbs energy models whose parameters are determined according to the type of binary system, i.e. partially or completely miscible, by using mutual solubility data and reliable vapor-liquid equilibrium data. If this was not the case, an option relies on the incorporation of binary data with some ternary information to calculate ternary liquid-liquid equilibrium data [21].

The calculation procedure of ternary liquid-liquid equilibrium data can be started by situating the position of the plait point, then, an estimation of the model parameters is realized using experimental vapor-liquid equilibrium data for the completely miscible binaries and few tie lines remote from the plait point [22]. Indeed, calculations of liquid-liquid equilibrium data for ternary systems with a plait point using just binary data would not provide adequate results, especially near the plait point. Accordingly, the distribution of a solute between liquid phases in the calculation of ternary or quaternary tie line data for systems exhibiting a plait point may not be accurate near to this critical point because all common excess Gibbs energy models do not give adequate results in this region [20]. Nevertheless, phase equilibrium calculations are required to simulate biphasic mixtures formed by two partially miscible or immiscible liquids. Due to that aspect, the liquid-liquid extraction process takes place. From a thermodynamic point of view, the presence of two liquid phases occurs when the Gibbs energy is diminished [23]. This means that a state of equilibrium between two liquid phases is reached and that the initial overall composition of a binary mixture is shared into two liquid compositions. When the Gibbs energy does not reach a minimum, the initial overall composition of a binary mixture is not shared into two liquid phase compositions.

Homogeneous mixtures in all proportions do not favor separation in the solvent extraction technique. Such a technique will be effective in separating components whose chemical properties resemble those of water or an organic solvent. In the case where the separation of components takes place from the aqueous to the organic layers, a third component added to an aqueous solution containing two or more components, including water, attracts to the organic phase the component whose properties are the most similar to its chemical properties than others [12]. Then, the distribution of that component begins to take place between both liquid phases. This distribution would continue until reaching a state of equilibrium between two liquid phases.

While the solute distribution between two liquid phases is mainly the most concerned in the liquid-liquid extraction process, however, this distribution concerns also the aqueous and organic solvents. Indeed, the two solvents would be distributed between its belonging phase and its non-belonging phase with different proportions, leading to a variation in the distribution ratios of solvent and cosolvent. These ratios are subject to change depending on the nature of mixtures and the conditions under which they were made. For instance, it was found that the presence of an electrolyte in a solvent mixture can affect the phase behavior of that mixture. As a result, the distributions of components between the two liquid phases can undergo significant modifications in their compositions. The presence of an electrolyte may overthrow the tendency of the behavior of a mixed-solvent toward a solute. Even an electrolyte would remain in one or other of the two phases, its presence in one phase would affect the liquid-liquid equilibrium compositions of mixtures. In some cases, the addition of an electrolyte is used to enhance the separation process and in others, the presence of an electrolyte can push a mixture to move from mixing to demixing behavior. Generally, the presence of an electrolyte can change the tendency of a mixture and therefore, the solubility of a solute may change more favorably in one phase than in the other.

1.4 Background and essence of the problem

1.4.1 Literature overview on aqueous speciation-phase equilibrium incorporation

The application of reliable models for the simulation of solute distributions between aqueous-organic mixtures requires reliable methods to distinguish different species that may exist in that mixture. Despite the considerable importance given to the research area related to the partition of organic solutes between water-organic solvents, an improvement based on the appropriate use of activity coefficient models remains necessary by exploiting their useful characteristics for treating mixtures included both neutral and ionic species.

While it is not common to take into account the dissociation of organic acids in the aqueous phase, this consideration should be retained when extracting them from the aqueous layer using solvent extraction processes. Chemical equilibrium can play a crucial role in separation processes. Such processes may include different types of chemical reactions and their considerations are required to manage better chemical separations [24]. This serves a useful intention to understand the effect of chemical reactions that occur in one phase or a solution on the multiphase behavior of mixtures. The consideration of species resulting from the dissociation of a solute in one phase affects its distribution between two immiscible liquid phases. If this case is adopted, a change in the equilibrium distribution of a solute is expected and this distribution is an effective coefficient compared to the case where no chemical reactions are considered. Organic solutes are characterized as weak acids or bases and their transfer from the aqueous phase to the organic phase recognize a partial dissociation in the aqueous solution. Practically, an organic solute can take other different forms in many mixtures based on the solvent extraction process. These forms include both undissociated and dissociated species. Only the undissociated form would be extracted in the organic phase whereas this form would undergo a partial dissociation in the aqueous phase [25].

Besides the physical phase equilibrium, the chemical equilibrium should be taken into account for two-phase mixtures. This consideration is required to clarify further the physical-chemical aspects of components that need to be extracted via solvent extraction processes. Furthermore, the consideration of ionic species brings the behavior of a system to an essential state that can be widely encountered in solvent extraction processes like electrolyte systems [26]. This is a proof case, for instance, weak electrolytes react with water to form both molecular and ionic species. Thus, a mere hypothesis based on the absence of dissociation of organic solutes in their aqueous solutions is not thermodynamically consistent.

The phase equilibrium and chemical speciation could be incorporated into thermodynamic calculations for a better description of the phase behavior of mixed-solvent electrolyte systems. Useful methods for the determination of thermodynamic properties in aqueous-organic electrolyte mixtures should combine an excess Gibbs energy model with information about the dissociation equilibrium of species included in these mixtures. This relies on the knowledge of species that may exist in an aqueous solution and on the identification of different chemical equilibrium that may occur in that solution. Although taking into account species contained in aqueous solutions, including ions, would lead to pronounced deviations in equilibrium compositions between liquid phases from those where the consideration of chemical speciation is ignored, the ability of an excess Gibbs energy model can be checked in the reproduction of equilibrium data for this purpose.

Approaches for treating phase and chemical equilibrium problems

The coupling of the chemical and physical equilibrium can be implemented in the modeling of liquid-liquid equilibrium for two-phase mixtures holding organic acids that would be necessarily partitioned between an aqueous phase and an organic phase to account for the overall phase equilibrium of mixtures. Such mixtures whose phase equilibrium calculations are related to the chemical speciation in aqueous solution would be affected [27-28]. The development of efficient approaches for calculating the thermodynamic properties of electrolyte solutions relies on the characterization of different difficulties that may be encountered due to ionic interactions, short-range interactions and chemical equilibrium between neutral and ionic species. Combining phase equilibrium calculations with speciation calculations corresponding to the chemical equilibrium between solution species needs to be performed in describing the phase behavior of mixed-solvent electrolyte systems [29].

Phase equilibrium models for mixed-solvent electrolyte mixtures are generally based on combining approaches originally designed for nonelectrolyte solutions with those that account for electrostatic effects between ions. The latter represent interactions between ions while the former describe short-range interactions. These two contributions are attributed to excess Gibbs energy models for electrolyte solutions. The development of these models recognizes classifications according to the method used in the treatment of electrolyte solution chemistry. The available electrolyte models can be classified into three categories. Two categories of models assume that electrolytes can be treated as dissociated or undissociated components in solutions. Some other models rely on the treatment of the solution chemistry by taking into account speciation calculations [30-31]. Hypotheses based on the complete dissociation of electrolytes in solutions are widely adopted by large classes of existing electrolyte thermodynamic models. When model approaches rely on considering electrolytes as undissociated components, the thermodynamic treatment would resemble nonelectrolyte mixture models [31]. As a result, electrostatic effects between ions will be omitted during phase equilibrium calculations.

Chemical and phase equilibrium calculations can be combined when applying speciation-based models to determine thermodynamic properties in mixed-solvent electrolyte mixtures [31]. The effect of salts on the phase behavior of mixtures will be evaluated considering chemical speciation occurring in electrolyte solutions [30]. Indeed, model approaches based on the assignment of speciation in the treatment of the phase behavior of mixtures, when it is necessary to specify it [31], are practically more useful compared to those based on the negligence of the dissociation of an electrolyte in a solution [31]. The ignorance of treating the solution chemistry whose nonideality of electrolyte solutions is due mainly to the effect of its species causes shortcomings in the phase behavior description [30]. Furthermore, model approaches based on presuming that long-range interactions have little effect on the phase behavior are unable to indicate the correct limiting behavior attributed to the Debye-Hückel theory. Therefore, chemical equilibrium calculations are inappropriate in the case where an electrolyte is considered as undissociated component [31].

1.4.2 Literature overview on the selection of a reference state

Reference state adopted by authors in their works

In the application of electrolyte models in mixed-solvent, an important matter is related to the selection of the most appropriate reference state for ionic activity coefficients. According to the McMillan-Mayer framework, the Debye-Hückel theory presents a mixed-solvent solution of a salt as an effective one-component system. Following this theory, and while the mixed solvent appears only as a dielectric medium, the reference state of ions is always the infinite dilution in the dielectric medium [32-33]. This reference state depends on the composition when mixtures contain more than one solvent. To represent the short-range interactions, the excess Gibbs energy models, like UNIQUAC and NRTL, use the pure liquid at the system temperature and pressure as the reference state [30]. Different reference states are commonly used for solvents and ionic species in the modeling process of mixed-solvent electrolyte mixtures. The infinite dilution in the dielectric medium (unsymmetrical reference state) is assigned for ionic species i.e. the infinite dilution in pure water or in a mixed-solvent. The pure liquid is designed as the reference state for solvents [30]. In the case where the electrostatic contribution is not considered, only the symmetrical convention is used for all components [30]. Electrolyte models based on the excess Gibbs energy combine an electrostatic interaction term (long-range contribution) and a short-range interaction term (short-range contribution). The latter must be normalized to an unsymmetrical convention for all ions i.e. the infinite dilution in pure water or in a mixed-solvent. The use of different reference states for contributions may turn up problems in the calculation of liquid-liquid equilibrium and salt solubility [32].

Zerres and Prausnitz [33] used the infinite dilution in pure water as the ionic reference state for both short-range and long-range contributions. The adoption of a hypothetical ideal dilute solution at unit mole fraction in water as the standard state for ions is always selected and applies to liquid-liquid equilibrium calculations for a ternary mixture or a water-free organic solvent mixture.

To move from one reference state to another, an additional term called the Born equation is used for this purpose. While this equation gives inadequate results compared to experimental data [33], Liu and Watanasiri [34] have added another term, called Brønsted-Guggenheim, to overcome these inadequacies. However, problems would arise in the calculation of liquid-liquid equilibrium for water-alcohol solvent mixture containing an electrolyte whose solubility is low in the solvent-rich phase. The hypothesis based on electrolytes-free organic phase may be adopted to cross such problems [34].

Zuo et al. [32] applied an equation of state (EoS) to model liquid-liquid equilibrium for mixed-solvent electrolyte systems. In their study, an extension of the work of Fürst and Renon [35] is presented, and the Born term is added to correct the standard state of ions. Although the Born term does not contribute to the solvent fugacity coefficients and ionic activity coefficients at the reference state of the infinite dilution in the solvent medium, its utility appears important in the calculation of liquid-liquid equilibrium and salt solubility [32]. Zuo et al. [32] have assumed that there is a second way to establish the reference state of ions by using the infinite dilution in the mixed solvent as the ionic reference state in the short-range and long-range contributions. The conversion of the mean activity coefficients at the reference state of the infinite dilution in the mixed solvent is made to those at the reference state of the infinite dilution in pure water through a term that takes into account the transfer from one reference state to another [32]. Although the Born term is less accurate in representing data, its physical contribution seems useful to unify the same reference state for the short-range and long-range contributions [36-37].

In the liquid-liquid equilibrium, the adoption of the same reference state in both liquid phases for ionic species and solvent molecules is required to avoid inconsistent data. The pure liquid at the system temperature and pressure is usually used for solvents as the reference state for both liquid phases. While this is quite difficult to be satisfied for ions according to the Debye-Hückel theory which considers a mixed-solvent as a dielectric medium, the selection of the same reference state in the two liquid phases for ionic species is not applicable following this assumption. In this case, the dielectric medium depends on the solvent compositions. While they are different from each other in the two liquid phases, different reference states would be encountered [34]. The Born equation was added to account for the transition of ionic species from a mixed-solvent infinite dilute reference state to an aqueous infinite dilute reference state [34]. Regardless of the solvent compositions, and by taking into account the Born equation, the infinite dilution in water will take place as the ionic reference state in the two liquid phases [34].

Reference state adopted in this work

The liquid-liquid separation process involves transferring components from one layer to another. The partition of a weak organic acid between two liquid phases includes its different forms. Chemical reactions in an aqueous solution containing a weak electrolyte would take place, leading to the appearance of new species resulting from the molecular solute. If no chemical equilibrium is considered, then only the molecular form of an organic acid will be partitioned between both liquid phases. However, this form of weak electrolyte in the aqueous solution may be modified. When it reacts with water, a weak electrolyte dissociates partially. As a result, solute molecules and ionic species are presented in that phase. While the distribution of a weak organic acid occurs between the aqueous and organic layers, the consideration of a partial dissociation in the aqueous layer may alter this tendency and may complicate the selection of ionic reference state. Nevertheless, ionic species result from the reaction of a weak electrolyte with water in the aqueous layer, and in general, the infinite dilution in water is adopted as the reference state for ions. The selection of the same reference state for ionic species in aqueous-organic solvent mixtures seems to be impossible unless if an additional term is included to account for transferring ions from the dielectric medium which depends on water-composition to the dielectric medium which depends on organic solvent-composition. This leads to adjust further parameters and makes the phase behavior description of multisolvent electrolyte mixtures more difficult. The adoption of the infinite dilution in pure water seems to be convenient as the reference state for ions in the two liquid phases [38].

1.5 Literature status

The knowledge of equilibrium compositions between an organic phase and an aqueous electrolyte solution is important for the design and optimization of separation processes. The topic related to the study and determination of liquid-liquid equilibrium data between aqueous and organic layers through excess Gibbs energy models for mixtures containing organic acids has been received major emphasis in the literature research works, but, further consideration should be attributed for suitable application of these models according to the types of mixtures. The basis of electrolyte thermodynamic models whose development was based on the thermodynamics of electrolyte solutions must contribute to the study of natures and factors that can lead to a nonideal behavior of mixtures.

The description of the phase equilibrium for electrolyte systems has become a crucial topic attracting several research works. The study of liquid-liquid equilibrium in mixed-solvent electrolyte systems has been received less attention compared to the representation of thermodynamic properties through experimental measurements and modeling framework of vapor-liquid equilibrium in mixed electrolyte aqueous solutions or in mixed-solvent electrolyte mixtures. However, there are excellent works interested in studying the effect of electrolytes on aqueous-organic solvent mixtures. In the following, a selected list of these works related to this research area is confined to the list below:

Liu and Watanasiri [34] have studied the representation of liquid-liquid equilibrium for water+alcohol+salt systems by using three contributions of the electrolyte NRTL model reported in [39]. In addition, the Brønsted-Guggenheim term was added to account for the inadequacies of the Debye-Hückel and Born terms in the case of mixed-solvent electrolyte systems;

A semiempirical thermodynamic method has been developed by Zerres and Prausnitz [33] to calculate ternary liquid-liquid equilibrium for systems containing water, an organic solvent and a salt. The model includes an extended Debye-Hückel equation to take into account the long-range electrostatic forces between ions, an extended equation of the Van Laar form to describe water–cosolvent nonideality and a chemical equilibrium method to account for short-range forces between solvent and ion;

Wang et al. [28] have studied the effect of electrolytes on liquid-liquid equilibrium in mixed-solvent electrolyte systems. The model consists of the Pitzer-Debye-Hückel term to account for the long-range interaction contribution, a short-range term to describe intermolecular interactions and a middle-range term to account for interactions between ions that are not considered by the Pitzer-Debye-Hückel term. Speciation calculations were taken into account in the calculation of liquid-liquid equilibrium. The solubilities of benzene in aqueous solutions of NaCl and $(NH_4)_2SO_4$

as well as the solubilities of benzene-cyclohexane in aqueous solutions of NaCl were presented. The solubilities of water in benzene were also given for ternary system of water+benzene+NaCl;

The study of multicomponent liquid-liquid equilibrium for mixtures containing ionic liquids was applied by Simoni et al. [40]. Among thermodynamic models applied to describe ternary liquid-liquid equilibrium for mixtures including ionic liquids, a modification has been conducted to the electrolyte NRTL model (eNRTL) concerning the formulation of the model based on a symmetric reference state with assuming complete dissociation of an ionic liquid. As a result, four components are involved in a ternary system i.e. solvent, cosolvent, anion and cation. The liquid-liquid equilibrium data were predicted from binary parameters by using eNRTL, UNIQUAC and NRTL excess Gibbs energy models;

Zuo et al. [32] have been extended the aqueous electrolyte equation of state (AEEOS) of Fürst and Renon [35] to predict liquid-liquid equilibrium of water+organic solvent+salt ternary systems. The model includes a repulsive force contribution, nonelectrolyte short-range term, ionic short-range term, long-range term and Born term;

Peng et al. [41] used an equation based on regular solution theory and Debye-Hückel term to calculate ternary liquid-liquid equilibrium of water+alcohol+salt systems;

Van Bochove et al. [36] have modified the electrolyte NRTL expression to account for the difference in the dielectric constants when calculating liquid-liquid equilibrium in mixed-solvent electrolyte systems. This was carried out by considering a solvent composition-dependent dielectric constant. The model contains a Pitzer-Debye-Hückel contribution, a local composition NRTL contribution, a Born contribution and a modified Brønsted-Guggenheim contribution. The model was applied to several ternary and quaternary systems;

Cheluget et al. [42] have proposed an excess Gibbs energy model based on combining an extended Bromley equation to consider mixed-solvents in solutions, the Flory–Huggins theory to describe interactions between solvents in the presence of an electrolyte and a term based on the Mean Spherical Approximation (MSA) theory to account for transferring ions from the infinite dilution in pure water to the infinite dilution in water-alcohol mixture. The proposed model was applied to ternary systems containing water, alcohol and salt;

Copeman and Stein [43] have developed a perturbed Mean Spherical Approximation (MSA) equation of state that includes a hard-sphere contribution, Mean Spherical Approximation (MSA) theory to account for the electrostatic contribution and attractive force contributions. The equation can be applied to a completely dissociated electrolyte in water. The correlation of liquid-liquid equilibrium for water+aniline+salt ternary systems has been performed.

1.6 Thesis status

Although the existing methods in the literature concerning calculations of phase equilibrium data for mixtures containing organic acids have been presented useful contributions for this purpose, a thorough treatment was not envisaged to understand the influence of the unexpected presence of charged species on the equilibrium compositions of aqueous-organic solvent mixtures. Indeed, these studies were based on the experimental measurements and calculations related to the separation process of organic acids from aqueous solutions in their molecular state and the assumption of the presence of unexpected ionic species in these aqueous solutions was ignored. Even the partition of an organic acid between two liquid phases changes in favor of an organic phase, certain considerations must be taken into account. This appears to be important for evaluating the equilibrium distribution of organic acids. In fact, the most important criterion beyond this concern is to consider the thermodynamic nature of these organic components in their contact with water and the different states in which they would be in their aqueous solutions.

Even without any attempt in bringing into contact an organic liquid with an aqueous liquid to transfer an organic acid from the aqueous phase to the organic phase which are completely different from each other, a description of an aqueous solution is required to classify different species that may exist in that phase before any separation action from one solvent to another. The presence of ionic species yields the phase behavior more complicated. Such complexity depends mainly on the interactions between ions causing a deviation from the ideal behavior and making phase behavior description quite difficult. For this reason, theories developed for nonelectrolyte mixtures cannot be used to describe electrolyte mixtures.

In most cases, nonideal behavior is often encountered in separation processes causing difficulties and affecting the mass transfer of the phases in contact. A particular contribution should be given in obtaining properties and representing the phase behavior of mixtures exhibiting a nonideal behavior.

A key to this issue can be depicted through excess Gibbs energy models for assessing the effect of ionic species contained or introduced into aqueous organic acids solutions-organic solvent mixtures. Such mixtures whose phase behavior will be different from the original one will require a thermodynamic treatment of the phase equilibrium adapted to mixed-solvent electrolyte mixtures. For a suitable treatment, both physical and chemical contributions need to be considered to obtain data and evaluate the effect of ionic species on the equilibrium distributions of components. In practice, mixtures involving electrolytes are rather more complex than nonelectrolyte ones due to several phenomena. However, a quantitative description of these phenomena may be performed by referring to actual electrolyte thermodynamic models, such the Extended UNIQUAC model, for understanding the phase behavior of electrolyte mixtures.

We notice that no works in the open literature have been found treating a partial dissociation of organic acids in aqueous solutions and extends it to multicomponent aqueous-organic mixtures.

1.7 Thesis motivation

The separation of organic acids by the liquid-liquid equilibrium process is commonly used as a separation technique. The nonideal behavior reigns in the separation of multicomponent mixtures involving more than two phases in industrial chemical processes. Weak organic acids dissolve in water to form both ionic and molecular species. The ionic species result from a partial dissociation of the components that need to be separated from the aqueous phase to the nonaqueous phase. The presence of electrolytes causes discrepancies from nonelectrolyte mixtures leading to a nonideal thermodynamic behavior in the separation process of two-liquid phase mixtures. Such mixtures contain at least two solvents, organic components and species of aqueous solutions i.e. one aqueous solvent with one or two nonaqueous solvents, organic acids and ionic species are all considered to form different types of mixtures. These types of mixtures are of practical importance to study their phase behavior through a separation technique. The application of liquid-liquid equilibrium in a manner that considers the solution chemistry in describing the phase behavior of mixed-solvent with components that would be shared between two partially miscible liquids was found to have a practical application in chemical processes.

The determination of the phase equilibrium of mixed-solvent electrolyte mixtures was linked to the solution chemistry by the identification of speciation. The calculation of speciation in aqueous solution was exploited to describe the liquid-liquid equilibrium behavior in mixed-solvent electrolyte mixtures. Mixed-solvent electrolyte mixtures may raise more difficulties compared to aqueous electrolyte solutions. Information about speciation can provide a useful support to understand which element will affect the separation of components. The consideration of the aqueous speciation in the thermodynamic modeling of multicomponent aqueous-organic mixtures constitutes a key element for better studying the thermodynamic behavior of electrolytes in mixed aqueous-organic solvents.

An adequate determination of the distribution of organic acids between two partially miscible liquids requires considering the physical and chemical equilibrium. This is a prerequisite to obtain realistic information about the mass transfer of multicomponent mixtures involved between the aqueous and organic phases. Indeed, there was a need for a thermodynamic model describing the requirement quoted above. The simulation of liquid-liquid equilibrium process for determining phase compositions of systems containing weak organic acids by considering a partial dissociation in their aqueous solutions is required to test the applicability of an electrolyte thermodynamic model in calculating equilibrium data outside experimental data ranges whose essential role is the validation of model calculations. In the thermodynamic modeling of liquid-liquid equilibrium, the nonideality caused by the presence of ionic species in the aqueous phase was taken into account. The Extended UNIQUAC model was used by considering chemical reactions occurring in the aqueous phase to improve the thermodynamic treatment of mixtures containing organic acids different from that available in the literature based on considering nonelectrolyte systems.

1.8 Thesis objectives

The research project was aimed to investigate the effect of charged species on the equilibrium compositions of organic acids between two liquid phases. The aqueous speciation was considered in the thermodynamic modeling of liquid-liquid equilibrium to test the capacity of the Extended UNIQUAC model in treating multicomponent electrolyte systems. Further, the predictive capability of the model was expanded to predict equilibrium phase compositions of ternary and quaternary systems from binary interaction parameters adjusted using the existing binary data from the literature. The research was also conducted to evolve the following purposes:

- To keep up-to-date with the literature by targeting research works related to the thermodynamics of electrolyte mixtures;
- To try to understand the particularity of the presence of electrolytes in separation processes;
- To try to understand the thermodynamic concepts of electrolyte solutions;
- To have an acquaintance in the existing thermodynamic models;
- To have an acquaintance in adjusting model parameters;
- To have an acquaintance in calculating liquid-liquid equilibrium and vapor-liquid equilibrium for binary, ternary and quaternary systems.

References

[1] Meissner, E. Phosphoric acid as an electrolyte additive for lead/acid batteries in electric-vehicle applications. J. Power Sources 67, 135–150 (1997).

[2] Zigová, J; Šturdík, E. Advances in biotechnological production of butyric acid. J. Ind. Microbiol. Biotechnol. 24, 153–160 (2000).

[3] Kijkowska, R.; Pawlowska-Kozinska, D.; Kowalski, Z.; Jodko, M.; Wzorek, Z. Wet-process phosphoric acid obtained from Kola apatite. Purification from sulphates, fluorine, and metals. Sep. Purif. Technol. 28, 197–205 (2002).

[4] King, J. M.; Kunz, H. R. Phosphoric acid electrolyte fuel cells. Handb. Fuel Cells (2010).

[5] Uslu, H.; Kirbaşlar, Ş. I. Extraction of aqueous of malic acid by trioctylamine extractant in various diluents. Fluid Phase Equilib. 287, 134–140 (2010).

[6] Senol, A. Liquid-liquid equilibria for the system (water + carboxylic acid + chloroform): Thermodynamic modeling. Fluid Phase Equilib. 243, 51–56 (2006).

[7] Marco, J. M.; Galan, M. I.; Costa, J.. Liquid-liquid equilibria for the quaternary system water-phosphoric acid-1-hexanol-cyclohexanone at 25. degree. C. J. Chem. Eng. Data. 33, 211–214 (1988).

[8] Ruiz, F.; Galan, M. I; Boluda, N. Quaternary liquid-liquid equilibrium: Water-phosphoric acid-1-butanol-2-butanone at 25°C. Fluid Phase Equilib. 146, 175–185 (1998).

[9] McCullough, J. F; Frederick, L. L.. Purification of phosphoric acid with methanol and ammonia. J. Agric. Food Chem. 24, 180–187 (1976).

[10] Kırbaşlar, Ş. İ.; Şahin, S.; Bilgin, M. (Liquid + liquid) equilibria of (water + propionic acid + diethyl succinate or diethyl glutarate or diethyl adipate) ternary systems. J. Chem. Thermodyn. 39, 1463–1469 (2007).

[11] Ghanadzadeh, H.; Ghanadzadeh, A.; Asgharzadeh, S. ;Dastmoozeh, N. Phase diagrams for the aqueous solutions of butyric acid with cyclohexane at different temperatures: Experimental and correlated data. Thermochim. Acta 523, 154–160 (2011).

[12] Liu, C. K. Group-contribution methods in estimating liquid-liquid distribution coefficients (Doctoral dissertation, Texas Tech University) (1981).

[13] Stevens, G. W.; Lo, T. C.; Baird, M. H. Extraction, liquid-liquid. Kirk-Othmer Encyclopedia of Chemical Technology (2000).

[14] Lo, T. C.; Baird, M. H. Extraction, Liquid–Liquid. Kirk-Othmer Encyclopedia of Chemical Technology (2000).

[15] Cockrem, M. C. M.; Flatt, J. H.; Lightfoot, E. N. Solvent Selection for Extraction from Dilute Solution. Sep. Sci. Technol. 24, 769–807 (1989).

[16] Schwartzentruber, J.; Renon, H.; Watanasiri, S. Development of a new cubic equation of state for phase equilibrium calculations. Fluid Phase Equilib. 52, 127–134 (1989).

[17] Sørensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, A. Liquid-liquid equilibrium data: Their retrieval, correlation and prediction Part II: Correlation. Fluid Phase Equilib. 3, 47–82 (1979).

[18] García-Sánchez, F.; Schwartzentruber, J.; Ammar, M. N.; Renon, H. Modeling of multiphase liquid equilibria for multicomponent mixtures. Fluid Phase Equilib. 121, 207–225 (1996).

[19] Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems. AIChE J. 21, 116–128 (1975).

[20] Lee, B. H.; Qin, Y.; Prausnitz, J. M. Thermodynamic representation of ternary liquid-liquid equilibria near-to and far-from the plait point. Fluid Phase Equilib. 240, 67–72 (2006).

[21] Anderson, T. F.; Prausnitz, J. M. Application of the UNIQUAC Equation to Calculation of Multicomponent Phase Equilibria . 2 . Liquid-Liquid Equilibria. Ind. Eng. Chem. Process Des. Dev. 17, 561–567 (1978).

[22] De Pablo, J. J.; Prausnitz, J. M. Thermodynamics of liquid-liquid equilibria including the critical region. AIChE J. 34, 1595–1606 (1988).

[23] Olaya, M. D. M.; Reyes-Labarta, J. A.; Serrano Cayuelas, M. D.; Marcilla, A. Vapor-liquid equilibria: Using the gibbs energy and the common tangent plane criterion. Chem. Eng. Educ. 44, 236–244 (2010).

[24] Treybal, R. E. Methods of Calculation II. Stagewise Contact, Multicomponent Systems. Liquid Extraction, 2nd Edition, McGraw-Hill Book Company, New York, 275-276 (1963).

[25] Sirkar, K. K. Separation of Molecules, Macromolecules and Particles. Principles, Phenomena and Processes. Cambridge University Press (2014).

[26] Bart, H. J. Reactive extraction. In Reactive Extraction. Springer, Berlin, Heidelberg (2001).

[27] Wang, P.; Springer, R. D.; Anderko, A.; Young, R. D. Modeling phase equilibria and speciation in mixed-solvent electrolyte systems. Fluid Phase Equilib. 222, 11–17 (2004).

[28] Wang, P.; Anderko, A.; Springer, R. D.; Young, R. D. Modeling phase equilibria and speciation in mixed-solvent electrolyte systems: II. Liquid-liquid equilibria and properties of associating electrolyte solutions. J. Mol. Liq. 125, 37–44 (2006).

[29] Kosinski, J. J.; Wang, P.; Springer, R. D.; Anderko, A. Modeling acid-base equilibria and phase behavior in mixed-solvent electrolyte systems. Fluid Phase Equilib. 256, 34–41 (2007).

[30] Wang, P.; Anderko, A.; Young, R. D. A speciation-based model for mixed-solvent electrolyte systems. Fluid Phase Equilib. 203, 141–176 (2002).

[31] Anderko, A., Wang, P. & Rafal, M. Electrolyte solutions: From thermodynamic and transport property models to the simulation of industrial processes. Fluid Phase Equilib. 194, 123–142 (2002).

[32] Zuo, J. Y.; Zhang, D.; Fürst, W. Predicting LLE in mixed-solvent electrolyte systems by an electrolyte EOS. AIChE J. 46, 2318–2329 (2000).

[33] Zerres, H.; Prausnitz, J. M. Thermodynamics of phase equilibria in aqueous-organic systems with salt. AIChE J. 40, 676–691 (1994).

[34] Liu, Y.; Watanasiri, S. Representation of liquid-liquid equilibrium of mixed-solvent electrolyte systems using the extended electrolyte NRTL model. Fluid Phase Equilib. 116, 193–200 (1996).

[35] Fürst, W.; Renon, H. Representation of excess properties of electrolyte solutions using a new equation of state. AIChE J. 39, 335–343 (1993).

[36] van Bochove, G. H.; Krooshof, G. J.; de Loos, T. W. Modelling of liquid-liquid equilibria of mixed solvent electrolyte systems using the extended electrolyte NRTL. Fluid Phase Equilib. 171, 45–58 (2000).

[37] van Bochove, G. H.; Krooshof, G. J.; de Loos, T. W. Two- and three-liquid phase equilibria in the system water + 2-heptanone + caprolactam + ammonium sulfate: Experiments and modeling. Fluid Phase Equilib. 194-197, 1029–1044 (2002).

[38] van Bochove, G. H. Two- and three-liquid phase equilibria in industrial mixed-solvent electrolyte solutions: Experiments and modelling of systems of importance for the extraction of caprolactam (2004).

[39] Aspen Technology. Inc., ASPEN PLUS Electrolytes Manual, Cambridge, MA (1988).

[40] Simoni, L. D.; Lin, Y.; Brennecke, J. F.; Stadtherr, M. A. Modeling liquid-liquid equilibrium of ionic liquid systems with NRTL, electrolyte-NRTL, and UNIQUAC. Ind. Eng. Chem. Res. 47, 256–272 (2008).

[41] Peng, Q.; Li, Z.; Li, Y. Application of regular solution theory to calculation of liquid-liquid equilibria for water-containing systems. Fluid Phase Equilib. 97, 67–80 (1994).

[42] Cheluget, E. L.; Marx, S.; Weber, M. E.; Vera, J. H. Equilibrium in biphasic aqueous systems: A model for the excess gibbs energy and data for the system H_2O-NaCl-1-propanol at 25°C. J. Solution Chem. 23, 275–305 (1994).

[43] Copeman, T. W.; Stein, F. P. A perturbed hard-sphere equation of state for solutions containing an electrolyte. Fluid Phase Equilib. 35, 165–187 (1987).

2. Thermodynamics and theories of electrolytes

2.1 Thermodynamic models

2.1.1 Introduction

The determination of the thermodynamic properties between two liquid phases at equilibrium is a fundamental task in the liquid-liquid equilibrium process. This would require calculation methods based on a modeling framework to obtain a thermodynamically stable state for mixtures and represent their properties at that state. The specific way of designing such properties relies on the development of thermodynamic models adapted to the types of mixtures. The description of the phase behavior of mixtures from limited experimental data using a reliable thermodynamic model that represents precisely equilibrium data is demanded. However, this depends on the availability of a comprehensive model able to represent equilibrium data and extend its applicability to the description of nonideal behavior. In this context, the development of thermodynamic models for modeling phase equilibrium mixtures is required to represent their phase diagrams. Before evoking thermodynamic models that have been proposed to describe the phase behavior of electrolyte systems, it is primarily desirable to mention thermodynamic models that have been introduced to treat nonelectrolyte systems.

2.1.2 Thermodynamic models for nonelectrolyte systems

In the following, thermodynamic models for nonelectrolyte systems confined to Wilson, NRTL, UNIQUAC and UNIFAC models are presented below.

2.1.2.1 Wilson model

Wilson [1] proposed a thermodynamic model to represent properties between the vapor and liquid phases for various polycomponent mixtures of nonelectrolytes. The proposed model was based on the local composition concept. The principle relies on the assumption that the composition of the system in the neighborhood of a given molecule differs from that of the bulk composition due to the effect of intermolecular forces [2]. Due to that effect, the mixing of molecules is nonrandom [3]. The Wilson model contains two adjustable parameters for a binary mixture. The prediction of ternary vapor-liquid equilibrium properties from binary data was successfully accomplished. However, a supplementary parameter may be added to obtain a good fit for immiscible liquid mixtures. The excess Gibbs energy is given as follows [3]:

$$\frac{G^E}{RT} = -\sum_i x_i \ln\left(\sum_j A_{ij} x_j\right) \qquad \textbf{(2-1)}$$

x_i is the mole fraction of component (i) and A_{ij} are the adjustable parameters.

2.1.2.2 NRTL model

The Nonrandom Two-Liquid (NRTL) model was proposed by Renon and Prausnitz [4] to represent a new expression based on Scott's two-liquid theory and on the approach of nonrandomness in liquid mixtures analogue to that adopted by Wilson [1]. According to Scott's two-liquid theory, there are two kinds of cells for components of a binary mixture i.e. one for molecules (i) and one for molecules (j). Further, the molecules are distributed in a nonrandom way. The model contains two adjustable parameters and a third parameter to account for the nonrandomness effect in liquid mixtures. This parameter can be fixed or adjusted depending on the availability of data. The model can be applied to represent equilibrium properties between vapor-liquid and liquid-liquid phases. The excess Gibbs energy is given as follows [4]:

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} \tag{2-2}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \text{ and } \tau_{ji} = \left(\frac{g_{ji} - g_{ii}}{RT}\right)$$

x_j is the overall mole fraction of component (j), g_{ij} are energies of interaction between an (i-j) pair of molecules, G is a coefficient and α is the nonrandomness parameter. T is the absolute temperature and R is the gas constant.

2.1.2.3 UNIQUAC model

Abrams and Prausnitz [5] proposed a new semi-theoretical equation for the excess Gibbs energy developed from a statistical-mechanical basis. The Universal Quasi-Chemical (UNIQUAC) model takes into account the difference in size and shape of molecule mixtures. Like Wilson [1] and NRTL [4] models, UNIQUAC model is based on the local composition concept by introducing the so-called local area fraction as the primary concentration variable that could be a more appropriate parameter for mixtures whose molecules are widely different in size and shape. The model consists of a combinatorial term and residual term. The later takes into account the interactions between molecules whereas the former takes into consideration the differences in molecular size and shape. Abrams and Prausnitz [5] applied their model to vapor-liquid equilibrium and liquid-liquid equilibrium for binary and multicomponent mixtures with only two adjustable parameters per binary. The excess Gibbs energy is given as follows [5]:

$$\frac{G^E}{RT} = \frac{G^E_{Com}}{RT} + \frac{G^E_{Res}}{RT} \tag{2-3}$$

$$\frac{G^E}{RT} = \sum_i x_i \ln\left(\frac{\varphi_i}{x_i}\right) - \frac{Z}{2}\sum_i q_i x_i \ln\left(\frac{\varphi_i}{\theta_i}\right) - \sum_i q_i x_i \ln\left(\sum_j \theta_j \tau_{ji}\right)$$

$$\tau_{ji} = \exp\left(-\frac{\left(U_{ji} - U_{ii}\right)}{RT}\right) \tag{2-4}$$

G^E_{Com} G^E_{Res} are the combinatorial and residual terms, respectively. φ_i and θ_i are segment and area fractions of component (i), respectively. x_i is the mole fraction and q_i is the area parameter of component (i). Z is the lattice coordination number fixed at 10. U_{ji} is UNIQUAC binary interaction parameter.

2.1.2.4 UNIFAC model

Fredenslund et al. [6] proposed a model to predict the activity coefficients for nonelectrolyte liquid mixtures. The UNIQUAC Functional-group Activity coefficients (UNIFAC) model was consisted to combine an extension of the quasi chemical theory of liquid mixtures (UNIQUAC) with the solution-of-functional-groups concept. The main idea of the development of the method presented by Fredenslund et al. [6] relies on considering that the number of chemical compounds of interest in chemical technology is much greater than that of functional groups constituting these compounds. Consequently, if a physical property of a fluid is considered to be the sum of contributions attributed by the molecule’s functional groups, it is possible to correlate properties for a large number of fluids with a restraint number of parameters which characterize the contributions of individual groups. The combinatorial activity coefficient term reported by Abrams and Prausnitz [5] has been used directly whereas the residual activity coefficient term is modified by introducing the solution-of-groups concept given by the equation (2-5). The resulting model contains two adjustable parameters per pair of functional groups. The model can be applied to binary and multicomponent mixtures. This has been confirmed for a large number of mixtures containing water, hydrocarbons, alcohols, chlorides, nitriles, ketones, amines and other organic fluids for a temperature range of 275°-400°K.

$$\ln\gamma_i^{Res} = \sum_k \varsigma_k^i \left[\ln\left(\Gamma_k\right) - \ln\left(\Gamma_k^i\right)\right] \tag{2-5}$$

Γ_k is the group residual activity coefficient and Γ_k^i is the residual activity coefficient of group (k) in a reference solution containing only molecules of type (i). ς_k^i is the number of groups of kind (k) in a molecule (i).

2.1.3 General highlights of electrolyte solutions

The electrolyte solutions are ubiquitous in many chemical process applications. They have specific properties and their roles in chemical industries are very important. Due to that implication, research studies related to electrolyte solutions have increased during the last decades. Among research areas for which electrolyte solutions have received marked attention including desalination of seawater, environment, salting-in and salting-out effects and other research fields.

The electrolyte solutions present specific characteristics different from those of nonelectrolyte solutions. The most apparent characterization which leads to distinguish between electrolyte solutions and nonelectrolyte solutions is the presence of molecular and ionic species. When a solution is free of ions or in other words, when a solute molecule does not separate into cations and anions, the solution is a solution of nonelectrolyte. Electrolytes can be classified into two categories according to their degree of dissociation. Electrolytes whose dissociation is complete into cations and anions are called strong electrolytes while electrolytes whose dissociation is partial are called weak electrolytes leading to the presence of undissociated solute molecules and ionic species in the same solution. Such a type of solution raises many difficulties caused by different types of interactions. The presence of ionic species has significant effects in bringing a solution from the ideal to nonideal thermodynamic behavior. As a result, electrostatic forces are responsible for large deviations from the ideal behavior in electrolyte solutions. In addition to interactions between ions, electrolyte solutions recognize other types of interactions between components involved. These types of interactions include:

- The long-range forces are electrostatic forces due to the presence of charged species in a solution. These forces are inversely proportional to the square of the distance between ions;
- The short-range forces are forces that occur over a short distance between ions and solvent molecules. The interactions between molecules are also referred to as short-range forces.

Electrolyte solutions exhibit complex behavior compared to nonelectrolyte solutions. For instance, a solution of water and an electrolyte whose dissociation is complete and therefore, the solution consists of cations and anions in addition to the water molecules. Further to these species, undissociated electrolyte molecules are also presented in an aqueous solution if the dissociation is incomplete. The most important is the choice of a precise model to describe the thermodynamic properties of electrolyte solutions.

Numerous theoretical, empirical and semi-empirical studies have attempted to develop thermodynamic models able to take into account interactions between different species by establishing both molecular and ionic activity coefficients. Several thermodynamic models have been established to describe the phase equilibrium of electrolyte systems by proposing extended versions of nonelectrolyte models. The extension of nonelectrolyte models to electrolyte models was carried out by considering the excess Gibbs energy of electrolyte solutions as the sum of two contributions. One contribution represents the long-range electrostatic interactions while the second is to account for the short-range interactions.

2.1.4 Thermodynamic models for electrolyte solutions

In the following, a short review of some kinds of electrolyte thermodynamic models proposed in the literature will be given here. This will cover models that take into account the long-range forces as well as the short-range forces.

2.1.4.1 Debye-Hückel model

A theoretical model was introduced by Debye-Hückel [7] to describe the long-range electrostatic forces. This was the first electrolyte thermodynamic model developed to take into account the interaction between ions. Its theoretical base has been immensely adopted in many research works and still has a fundamental contribution to the development of thermodynamic models for electrolyte solutions. Among fundamental assumptions adopted by Debye and Hückel [7] in developing their theory are: the solvent is replaced by a dielectric continuum, the short-range interactions between water molecules and ionic species are not considered, and only the long-range electrostatic interactions are described by the model. Another important assumption whose physical validity is reasonable at high dilution and not at high ionic concentrations where the short-range forces become dominant is to consider that large deviations from ideality are mainly caused by electrostatic interactions between ions. Fowler and Guggenheim [8] suggested the following expression for the electrostatic contribution to the excess Gibbs energy:

$$\frac{G^E_{D-H}}{RT} = -x_W M_W \frac{4A}{b^3}\left[\ln(1+b\sqrt{I}) - b\sqrt{I} + \frac{b^2 I}{2}\right] \qquad \textbf{(2-6)}$$

x_w and M_W are the mole fraction and the molecular weight of water, respectively. $b = 1.5\,(\text{Kg mol}^{-1})^{1/2}$ is a constant. A is the Debye-Hückel parameter given by the following equation [8]:

$$A = \begin{bmatrix} 1.131 + 1.335*10^{-3}*(T-273.15) + \\ 1.164*10^{-5}*(T-273.15)^2 \end{bmatrix} \text{kg}^{1/2}\ \text{mol}^{-1/2} \qquad \textbf{(2-7)}$$

I is the ionic strength given by following equation:

$$I = \frac{1}{2}\sum_j z_j^2 m_j \qquad \textbf{(2-8)}$$

m_j is the molality (mol/kg H_2O) and z_j is the charge of ion (j).

2.1.4.2 Extension of Debye-Hückel model

Several models have been proposed to extend the applicability of the Debye-Hückel model [7] to various types of solutions. Robinson and Stokes [9] proposed to modify the equation of the Debye-Hückel [1]. The proposed model can be applied to high concentration solutions. An empirical model was proposed by Bromley [10] applicable to single and multicomponent strong aqueous solutions. The applicability of the model was tested by correlating activity and osmotic coefficients up to an ionic strength of six (mol/kg H_2O). The proposed model has one adjustable parameter. The equation of the activity coefficient is given by the following expression [10]:

$$\log\gamma_{\pm} = \frac{-A_{\gamma}\left|Z_{+}Z_{-}\right|\sqrt{I}}{1+\rho\sqrt{I}} + \frac{(0.06+0.6B)\left|Z_{+}Z_{-}\right|I}{\left(1+\frac{1.5}{\left|Z_{+}Z_{-}\right|}I\right)^{2}} + BI \qquad \textbf{(2-9)}$$

ρ is the distance of closest approach of ions in solution, $\left|Z_{+}Z_{-}\right|$ is the absolute value of the charge product, I is the ionic strength, $A_{\gamma} = 0.511\,kg^{1/2}\,mol^{-1/2}$ at 25°C is the Debye-Hückel constant for activity coefficient and B is the adjustable parameter.

Meissner and Tester [11] proposed an expression of the mean ionic activity coefficient that can be applied to a number of electrolytes. The applicability range of the proposed model is valid for an ionic strength of six and temperatures above 25°C.

Pitzer's model is widely used to describe the thermodynamic properties of electrolytes. In the next, a brief presentation of this model is given.

2.1.4.3 Pitzer Model

Pitzer [12] suggested an improvement of the Debye-Hückel model [7] by developing a model describing the thermodynamic properties of aqueous electrolytes. In his model, Pitzer considered it was extremely important to recognize that there is an ionic strength dependence of the effect of short-range forces in binary interactions. The excess Gibbs energy for a solution containing n_w kg of solvent and $n_i, n_j \ldots$ moles of solute species (i, j,...) is given as follows [12,13]:

$$\frac{G^{E}}{RT} = n_w f(I) + \frac{1}{n_w}\sum_{ij}\lambda_{ij}(I)\,n_i n_j + \frac{1}{n_w^{2}}\sum_{i,j,k}\mu_{ijk}\,n_i n_j n_k \qquad \textbf{(2-10)}$$

$f(I)$ is a modified Debye-Hückel term expressing the effect of the long-range electrostatic interactions which is given by the following equation [12,13]:

$$f(I) = -\frac{4A_{\varphi}I}{1.2}\ln\left(1+1.2\sqrt{I}\right) \qquad \textbf{(2-11)}$$

A_{φ} is the Debye-Hückel parameter which is defined as follows [13]:

$$A_{\varphi} = \frac{1}{3}\left(\frac{2\Pi\, N_0 d_w}{1000}\right)^{1/2}\left(\frac{e^2}{DKT}\right)^{3/2} \qquad \textbf{(2-12)}$$

D is the dielectric constant, e is the electrical charge, K is the Boltzmann constant, N_0 is the Avogadro number, T is the temperature and d_w is the density of water.

λ_{ij} μ_{ijk} are the binary and ternary short-range interaction terms, respectively. I is the ionic strength.

2.1.4.4 Pitzer-Debye-Hückel model

An extended version of the Debye-Hückel model [7] was proposed by Pitzer [14]. The model is applicable to solutions whose composition extends continuously from a dilute solution in water or another polar molecular solvent to a pure fused salt. The proposed model has only one adjustable parameter. The excess Gibbs energy is given as follows [14]:

$$\frac{G^E}{RT} = -\left(\sum n_k\right)\left(\frac{1000}{M_S}\right)^{1/2}\left(\frac{4A_{\varphi}I_X}{\rho}\right)\ln\left(1+\rho\sqrt{I_X}\right) \qquad \textbf{(2-13)}$$

n_k is the number of moles of species (k), M_s is the molecular weight of the solvent (s) and ρ is the closest approach parameter of the Pitzer-Debye-Hückel equation, this an adjustable parameter. A_{φ} is the Debye-Hückel constant which is given by the following expression [14]:

$$A_{\varphi} = \left(\frac{1}{3}\right)\left(\frac{2\Pi\, N_0 d_s}{1000}\right)^{1/2}\left(\frac{e^2}{DKT}\right)^{3/2} \qquad \textbf{(2-14)}$$

d_s is the density of the solvent (s), e is the electrical charge, D is the dielectric constant, K is the Boltzmann constant, N_0 is the Avogadro number and T is the temperature.

I is the ionic strength given by following equation:

$$I_X = \frac{1}{2}\sum_j z_j^2 x_j \qquad \textbf{(2-15)}$$

2.1.4.5 Mean Spherical Approximation (MSA)

Mean Spherical Approximation (MSA) is another type of thermodynamic models used to represent the electrostatic contribution. Like the Debye-Hückel theory [7], the Mean Spherical Approximation (MSA) theory is used to account for the long-range interaction forces between ions. The Mean Spherical Approximation (MSA) is a usual relation of belonging to the integral equation of Ornstein and Zernike [15]. The integral equation of Ornstein and Zernike is given as follows [15]:

$$h_{ij}\left(r_{ij}\right)=C_{ij}\left(r_{ij}\right)+\rho\int h_{kj}\left(r_{kj}\right)C_{ik}\left(r_{ik}\right)dr_k \qquad \textbf{(2-16)}$$

ρ is the density. $C_{ij}\left(r_{ij}\right)$ and $h_{ij}\left(r_{ij}\right)$ are the direct and indirect correlation functions for the pair of ions (i, j), respectively.

In Mean Spherical Approximation (MSA) theory, these functions satisfy the following conditions [16]:

$$\begin{cases} h_{ij}\left(r_{ij}\right)=-1 & \text{for } r_{ij}\le\sigma_{ij} \\ C_{ij}\left(r_{ij}\right)=-\dfrac{u_{ij}(r_{ij})}{KT} & \text{for } r_{ij}\succ\sigma_{ij} \\ \sigma_{ij}=\dfrac{\sigma_i+\sigma_j}{2} & \\ u_{ij}(r_{ij})=\dfrac{e^2Z_iZ_j}{Dr_{ij}} & \end{cases} \qquad \textbf{(2-17)}$$

r_{ij} is the distance between ion (i) and (j), σ_{ij} is the closest distance of approach for the pair of ions (i, j) and $u_{ij}(r_{ij})$ is the electrostatic interactive potential. e is the elementary charge and D is the dielectric constant.

For instance, a typical treatment of the electrostatic effects in electrolyte solutions through using Mean Spherical Approximation (MSA) is performed by Blum [16].

2.1.5 Local composition models

The short-range forces become dominant when electrolyte concentrations increase. The short-range forces include interactions between ions-molecules and molecules-molecules. The Debye-Hückel model and the Pitzer model in its general form are used to account for the long-range electrostatic forces. The consideration of all interactions between all components in mixed-solvent electrolyte systems needs to use models that take into account both short-range and long-range contributions. Semi-empirical models based on the local composition concept are used for this purpose. The long-range electrostatic forces between ions are presented by the Debye-Hückel or the Pitzer models while local composition models (such as NRTL and UNIQUAC) are used to account for the short-range forces.

2.1.5.1 NRTL model

Cruz and Renon [17] conducted the first work devoted to electrolyte solutions using the NRTL model. They proposed to represent the long-range forces using both the

Debye-Hückel and the Debye-McAulary theories and the short-range forces by the NRTL model. The model approaches were based to consider the pair of ions as undissociated molecules, and the free ions are regarded to be principally surrounded by solvent molecules. The resulting model contains four adjustable parameters and it was applied to correlate the mean ionic activity coefficient and the osmotic coefficient for binary aqueous solutions of partially or completely dissociated electrolytes at 298.15 K.

Chen et al. [18,19] proposed an electrolyte local composition model based on the NRTL model. In this model, the Pitzer-Debye-Hückel model [14] was used to represent the long-range forces and a new version of the NRTL model was developed to account for the short-range forces. Chen et al. [18,19] considered that there are three types of cells for a mixture consisting of a solvent and a completely dissociated electrolyte into cations and anions The modified version of the NRTL model was based on two main assumptions. The first assumes that the local composition of ions around ions of the same sign is zero (like-ion repulsion). This means that the repulsive forces between like-charged ions are extremely large. The second assumes that the distribution of cations and anions around a central solvent molecule is such that the net local ionic charge is zero (local electroneutrality). Two binary interactions were considered as adjustable parameters for a binary system of a solvent and a completely dissociated electrolyte. The validity of the model was demonstrated for various types of electrolyte systems. The excess Gibbs energy is given by the following expression [19]:

$$\begin{aligned}\frac{G^E}{RT} &= \sum_m X_m \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} \\ &+ \sum_c X_c \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{\sum_j X_j G_{jc,a'c} \tau_{jc,a'c}}{\sum_k X_k G_{kc,a'c}} \\ &+ \sum_a X_a \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{\sum_j X_j G_{ja,c'a} \tau_{ja,c'a}}{\sum_k X_k G_{ka,c'a}}\end{aligned} \qquad \textbf{(2-18)}$$

With,

$$X_j = C_j x_j \ (C_j = Z_j \text{ for ions and } C_j = 1 \text{ for molecules})$$
$$G_{ji} = \exp\left(-\alpha_{ji}\tau_{ji}\right)$$
$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \tag{2-19}$$
$$G_{ji,ki} = \exp\left(-\alpha_{ji,ki}\tau_{ji,ki}\right)$$
$$\tau_{ji,ki} = \frac{g_{ji} - g_{ki}}{RT}$$

α is the nonrandomness factor, x is the true liquid phase mole fraction of molecular and ionic species, X is the effective liquid phase mole fraction, g_{ij} and g_{ii} are energies of interaction between (j-i) and (i-i) species , G is a coefficient, T is the temperature and R is the gas constant.

Papaiconomou et al. [20] developed a model for which the Mean Spherical Approximation (MSA) theory for electrolyte solutions was combined with a modified version of the electrolyte NRTL model. The latter was used to account for the short-range interactions by rearranging some assumptions. The first assumption was based on considering that the number of cations and anions around a central solvent molecule is different. The second approach was to assume that an interaction parameter is linearly dependent on the solution composition. The resulting model has four adjustable parameters. Electrostatic forces due to the interaction between ions were represented by the MSA model. The model was applied to binary and ternary electrolyte solutions.

2.1.5.2 NRTL-NRF model

Haghtalab and Vera [21] followed the assumption proposed by Chen et al. [18,19] based on describing an aqueous electrolyte solution by the long-range interaction contribution and the short-range interaction contribution. The long-range forces due to the electrostatic interactions were represented by the Debye-Hückel theory while the short-range interactions were described by a new version of the NRTL model of Renon and Prausnitz [4]. The proposed model was formally similar to that published by Panayiotou and Vera [22]. The resulting model has two adjustable parameters per electrolyte. The applicability of the model was confirmed from dilute solution up to saturation. The obtained results were consistent by comparing with those obtained by Bromley [10], Meissner [11-23] and Chen et al. [18,19]. The excess Gibbs energy is given by the following expression [21]:

$$\frac{G^E}{RT} = \upsilon Z_A Z_C x_s^2 \left(\Gamma_E - 1\right)\lambda_E - x_w^2\left(\Gamma_w - 1\right)\lambda_w \tag{2-20}$$

Γ is the nonrandom factor, λ is the NRTL-NRF parameter and υ is the stoichometric number. Z_i is the absolute charge number of ionic species (i). x_i is the liquid mole fraction of component (i). T is the absolute temperature and R is the gas constant.

2.1.5.3 Wilson model

Zhao et al. [24] proposed to extend the Wilson model from the nonelectrolyte to aqueous electrolyte solutions by considering two contributions. The first contribution of the long-range electrostatic forces was described by the Pitzer-Debye-Hückel model [14]. To account for the short-range forces, a new expression based on the local composition concept was developed for the second contribution. Like Chen et al. [18,19]., Zhao et al. [24] assumed the existence of three kinds of local cells. These types of cells refer to cells with a central cation, cells with a central anion and cells with a central solvent molecule. In contrast to the extensions of the NRTL model to electrolytes available in the literature, the description of the short-range energy parameter between species in a local cell was quantified by an enthalpic rather than Gibbs energy nature. The model contains two adjustable parameters per water-electrolyte system. The accuracy of the model was tested for several single electrolyte systems in the representation of mean ionic activity coefficients for which the results were satisfied. The excess Gibbs energy is given by the following expression [24]:

$$\frac{G^E}{CRT} = -X_m \ln\left(\frac{X_m + \sum_k \left(X_{c_k} + X_{a_k}\right) H_{e_k m}}{X_m + \sum_k \left(X_{c_k} + X_{a_k}\right)}\right) - \sum_k X_{c_k}\left[\ln\left(\frac{X_m H_{me_k} + \sum_j X_{a_j} H_{e_j e_k}}{X_m + \sum_j X_{a_j}}\right)\right] - \sum_k X_{a_k}\left[\ln\left(\frac{X_m H_{me_k} + \sum_j X_{c_j} H_{e_j e_k}}{X_m + \sum_j X_{c_j}}\right)\right] \qquad \textbf{(2-21)}$$

$$H_{ij} = \exp\left(-\frac{E_{ij}}{CRT}\right) \qquad \textbf{(2-22)}$$

E is the dummy energy parameter, H is the dummy parameter, x is the mole fraction and X is the effective mole fraction. $C = 10$ is the coordination number, T is the absolute temperature and R is the gas constant.

A new development of the Wilson model was proposed by Xu and Macedo [25] to model the activity coefficients of electrolytes in aqueous solutions. The Pitzer-Debye-Hückel model [14] was used to represent the interactions between charged species. The expression of the short-range excess Gibbs energy proposed by Xu and Macedo [25] was similar to that of the Wilson model for nonelectrolytes. The resulting model has two adjustable parameters. The representation of the mean ionic activity coefficients of electrolytes was successfully described. The excess Gibbs energy is given by the following expression [25]:

$$\frac{G^E}{RT} = -\frac{1}{\alpha}\left[X_m \ln\left(X_m + \left(X_a + X_c\right)H_{em}\right) + X_c \ln\left(X_a + X_m H_{me}\right) + X_a \ln\left(X_c + X_m H_{me}\right)\right] \qquad \textbf{(2-23)}$$

$X_j = C_j x_j$ ($C_j = Z_j$ for ions and $C_j = 1$ for molecules)

α is the nonrandom factor, H is the enthalpy, x is the mole fraction and X is the effective mole fraction.

2.1.5.4 UNIQUAC model

The extension of the UNIQUAC model to electrolyte solutions was proposed by Christensen et al. [26]. The model includes two main contributions. The electrostatic interactions were described by a term based on the Debye-Hückel theory corrected by adding a term to account for mixed solvent systems. The UNIQUAC version published by Abrams and Prausnitz [5] was used as the second contribution of the model. The resulting model has two adjustable parameters per salt. The model was applied to completely dissociated electrolytes in pure and mixed solvents. The obtained results were well represented for binary water-salt systems at molalities up to 10 (mol/kg H_2O) and 6.5 (mol/kg H_2O) for 1:1 and 2:1 salts, respectively, as well as for the predicted water activities in mixed electrolyte solutions.

Sander et al. [27] proposed a modified version of the UNIQUAC model for mixtures with electrolytes. The contributions of the long-range electrostatic forces and the short-range forces were respectively represented by a term based on the Debye-Hückel theory and a modified UNIQUAC equation. They considered introducing concentration dependence in the interaction energy parameters between species. The model parameters were adjusted for alcohol-water mixtures containing different salts. The correlation and prediction of the salt effects on vapor-liquid equilibrium were conducted. Despite the large deviations in calculated pressures and temperatures, the model can be applied to study the salt effects on vapor-liquid equilibrium.

For the purpose to present a simplified version of the UNIQUAC model applied to electrolyte solutions, Nicolaisen et al. [28] proposed to modify the model developed by Sander et al. [27,29]. They considered model parameters to be concentration-independent to reduce the number of adjustable parameters. Further, temperature dependence of the model parameters was considered in the modified version of the Extended UNIQUAC model. Like Sander et al. [29], Nicolaisen et al. [28] used the Debye-Hückel equation suggested by Fowler and Guggenheim [8]. The results given by the model were well represented for both ternary solubility diagrams and vapor-liquid equilibrium data in the whole concentration range from infinite dilution to saturation.

The expression of the short-range excess Gibbs energy used in this thesis is generally similar to that used by Sander et al. [27,29] and Nicolaisen et al. [28] except the apparent difference depicted above in which they considered both concentration- and temperature-dependent model parameters.

2.1.5.5 UNIQUAC-NRF model

Haghtalab and Mokhtarani [30] proposed to extend the UNIQUAC-NRF model developed by Haghtalab and Asadollahi [31] to correlate liquid-liquid equilibrium of aqueous polymer-salt two-phase systems. This model was used to account for the effect of short-range interactions in aqueous two-phase systems. The long-range electrostatic forces were represented by a term based on the Debye-Hückel theory. The assumption based on the existence of four types of cells with a central solvent, polymer, cation or anion similar to that adopted by Chen et al. [18,19] and Haghtalab and Vera [21] is considered. The resulting model has six binary adjustable parameters for polymer-salt-water systems. The correlated results were consistent with the experimental data. The excess Gibbs energy is given by the following expression [30]:

$$\frac{G^E}{RT} = \frac{G^E_{Com}}{RT} + \frac{G^E_{Res}}{RT} \qquad \textbf{(2-24)}$$

$$\frac{G^E}{RT} = \sum_{i=1}^{n} x_i \ln\left(\frac{\varphi_i}{x_i}\right) + \frac{Z}{2}\sum_{i=1}^{n} x_i q_i \ln\left(\frac{\theta_i}{\varphi_i}\right) + \sum_{i=1}^{n} q_i x_i \left[\ln(\Gamma_{ii}) + \sum_{\substack{j=1 \\ j\neq i}}^{n} \theta_j \ln\left(\frac{\Gamma_{ji}}{\Gamma_{ii}}\right)\right]$$

$$\Gamma_{ij} = \tau_{ij}\Gamma_{jj}$$

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

$$a_{ij} = \frac{u_{ij} - u_{jj}}{R} \qquad \textbf{(2-25)}$$

$$\Gamma_{ii} = \frac{1}{\sum_{j\neq i(\text{forions})} \theta_j \tau_{ji}}$$

G^E_{Com} G^E_{Res} are the combinatorial and residual terms, respectively. x_i is the mole fraction and q_i is the surface parameter of component (i). Z is the coordination number fixed at 10. u_{ji} is the interaction parameters between (j-i). a_{ji} is the interaction parameters between (j-i). θ_i and φ_i , are the surface area and volume fractions of component (i), respectively. Γ is the nonrandom factor and τ is the Boltzmann factor.

2.1.5.6 UNIFAC model

Kikic et al. [32] suggested modifying the model proposed by Sander et al. [27]. The modification concerned a substitution of the UNIQUAC term by a UNIFAC term including group interaction parameters with no concentration dependence. A new estimation of group interaction parameters between ions and solvent groups was carried out. The proposed model contains three terms: a term based on the Debye-Hückel theory, and combinatorial and residual terms based on the UNIFAC contributions of Fredenslund et al. [33]. The model can be applied to predict the vapor-liquid equilibrium properties for solvent-water-salt mixtures.

Achard et al. [34] proposed an extension of the UNIFAC model for the correlation and prediction of salt effects on vapor-liquid equilibrium of mixed solvent systems. The model combines the model proposed by Pitzer [14], the modified UNIFAC group-contribution method proposed by Larsen et al. [35] and solvation equations to account for the hydration of ions by water molecules. Group interaction parameters between solvent groups were assumed to be temperature-dependent. The estimation of the interaction parameters between solvent groups and ions was made by adjusting the interaction energies suggested by Christensen et al. [26]. The application of the group-contribution method to alcohol-water-salt mixtures has shown a wide range of applicability compared to classical approaches based on UNIQUAC or NRTL models [34].

2.2 Thermodynamic properties of electrolyte solutions

2.2.1 Introduction

The treatment of electrolyte solutions contrasts sharply with that of nonelectrolyte solutions. Electrolyte solutions are characterized by specific properties due to the presence of ionic species that lead to obvious deviations from ideal behavior. The nonideal behavior of electrolyte solutions manifests by the presence of strong interaction forces between ions with each other and between ions and solvent molecules causing difficulties in the description of the liquid phase compared to the nonelectrolyte solution. Further, interaction forces between solvent molecules with each other and between solvent molecules and nonelectrolyte components are also presented in electrolyte solutions. Besides various types of interaction forces resulting in electrolyte solutions, concentration scales constitute also the main characteristics of the thermodynamics concepts of electrolyte solutions. Depending on the concentration scales of solution species, activity coefficients will recognize different bases. Consequently, the concepts of the thermodynamics of electrolyte solutions differ mainly from the thermodynamics of nonelectrolyte solutions. In the following, the important concepts of the thermodynamics of electrolyte solutions related to this thesis will be presented.

2.2.2 Concentration scales

As discussed previously, different concentration scales are used in electrolyte solutions. A liquid phase contain n_{so} moles of solvent (water) and n_s moles of a salt. The mole fractions of solvent (water) x_{so} and of ion x_j are defined as follows:

$$x_{so} = \frac{n_{so}}{n_{so} + n_s \sum_j \nu_j} \quad \textbf{(2-26)}$$

$$x_j = \frac{n_s \nu_j}{n_{so} + n_s \sum_j \nu_j} \quad \textbf{(2-27)}$$

$\sum_j$ represents the sum of all stoichiometric coefficients.

In electrolyte solutions, a useful concentration based on the molality scale $(\mathrm{mol/kg\ H_2O})$ is usually attributed. The molality of ion (j) is defined as follows:

$$m_j = \frac{\nu_j n_s}{n_{so} M_{so}} \quad \textbf{(2-28)}$$

M_{so} is the molecular weight of solvent.

The relation between the molality and the mole fraction of ionic species (j) is given as follows:

$$\frac{x_j}{m_j} = \frac{\dfrac{\nu_j n_s}{n_{so} + n_s \sum_j \nu_j}}{\dfrac{\nu_j n_s}{n_{so} M_{so}}} = x_{so} M_{so} \quad \textbf{(2-29)}$$

2.2.3 Concepts and basic terms of electrolyte solutions

In the mathematical formulation of the criteria of thermodynamic equilibrium between phases, the chemical potential that relates the concentration, the activity coefficient and the fugacity is used for this purpose. An aqueous solution contains n_s moles of salt and n_{so} moles of water by considering a total dissociation of salt into cations and anions. The expression of the Gibbs free energy of the solution at constant temperature and pressure is given by:

$$dG_{P,T} = \sum_i \mu_i dn_i = \mu_{so} dn_{so} + dn_s \sum_j \mu_j \nu_j \quad \textbf{(2-30)}$$

And;

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_{k \neq i}} \quad \textbf{(2-31)}$$

$\sum_j \nu_j$ are the stoichiometric coefficients. μ_j is the chemical potential of component (j) which is given by the following expression:

$$\mu_j = \mu^\circ{}_j + RT\ln(\frac{f_j}{f_j^\circ}) \qquad \textbf{(2-32)}$$

R is the gas constant, T is the absolute temperature and f_j is the fugacity of component (j) in the solution at a given temperature and pressure. $\mu^\circ{}_j$ and f_j° are the chemical potential and the fugacity of component (j) in the standard state, respectively.

Activity coefficients whose concentrations are based on the mole fraction and on the molality scales are called rational activity coefficients and molal activity coefficients, respectively. In electrolyte solutions, different conventions can be adopted for the activity coefficients of components. When adopting the symmetrical convention, the activity coefficient of solvent is unity in the pure component at a given temperature and pressure, while the activity coefficient of ionic species is unity at infinite dilution at a given temperature and pressure for the unsymmetrical convention.

The fugacity of solvent (i) is given as follows:

$$f_i = x_i \overset{\wedge}{\gamma}_i f_i^\circ \qquad \textbf{(2-33)}$$

$\overset{\wedge}{\gamma}_i$ and x_i are the symmetrical activity coefficient based on the mole fraction scale and the mole fraction of solvent (i), respectively.

The chemical potential of solvent (i) is given as follows:

$$\mu_i = \mu^\circ{}_i + RT\ln(x_i \overset{\wedge}{\gamma}_i) \qquad \textbf{(2-34)}$$

$\mu^\circ{}_i$ is the chemical potential of solvent (i) in its standard state

The fugacity of solute (j) with the mole fraction scale is given as follows:

$$f_j = x_j \bar{\gamma}_j H_{j,x} \qquad \textbf{(2-35)}$$

$\bar{\gamma}_j$ and $H_{j,x}$ are the unsymmetrical activity coefficient and the Henrys law constant of solute (j) based on the mole fraction scale, respectively.

The chemical potential of solute (j) with the mole fraction scale is given as follows:

$$\mu_j = \mu^*{}_j + RT\ln(x_j \bar{\gamma}_j) \qquad \textbf{(2-36)}$$

$\mu^*{}_j$ is the unsymmetrical chemical potential of solute (j) in the standard state based on the mole fraction scale.

The fugacity of solute (j) with the molality scale is given as follows:

$$f_j = m_j \gamma_j H_{j,m} \qquad \textbf{(2-37)}$$

γ_j and $H_{j,m}$ are the unsymmetrical activity coefficient and the Henrys law constant of solute (j) based on the molality scale, respectively.

The chemical potential of solute (j) with the molality scale is given as follows:

$$\mu_j = \mu^{\nabla}{}_j + RT\ln(m_j \gamma_j) \qquad \textbf{(2-38)}$$

$\mu^{\nabla}{}_j$ is the unsymmetrical chemical potential of solute (j) in the standard state based on the molality scale.

Regardless of the definition of the standard state and the concentration unit, the chemical potential of ionic species can be expressed in three forms below [36]:

$$\begin{cases} \mu_j = \mu^{\circ}{}_j + RT\ln(x_j \hat{\gamma}_j) & \text{(a)} \\ \mu_j = \mu^{*}{}_j + RT\ln(x_j \bar{\gamma}_j) & \text{(b)} \\ \mu_j = \mu^{\nabla}{}_j + RT\ln(m_j \gamma_j) & \text{(c)} \end{cases} \qquad \textbf{(2-39)}$$

By inserting equations (2-34) and (2-39) (a), the Gibbs free energy (equation (2-30)) takes the form:

$$G_{P,T} = \mu_{so} n_{so} + n_s \sum_j \mu_j \nu_j = n_{so}\left(\mu^{\circ}{}_i + RT\ln(x_i \hat{\gamma}_i) \right) + n_s \sum_j \nu_j \left(\mu^{\circ}{}_j + RT\ln(x_j \hat{\gamma}_j) \right) \qquad \textbf{(2-40)}$$

For an ideal solution, $\hat{\gamma}_i = \hat{\gamma}_j = 1$, and the equation (2-40) becomes:

$$G^{id}_{P,T} = n_{so}\left(\mu^{\circ}{}_i + RT\ln(x_i)\right) + n_s \sum_j \nu_j \left(\mu^{\circ}{}_j + RT\ln(x_j)\right) \qquad \textbf{(2-41)}$$

By subtracting the equation (2-40) from the equation (2-41), the excess Gibbs free energy is given as follows:

$$\frac{G^{E}{}_{P,T}}{RT} = \frac{G_{P,T} - G^{id}_{P,T}}{RT} = n_{so}\ln(\hat{\gamma}_i) + n_s \sum_j \nu_j \ln(\hat{\gamma}_j) \qquad \textbf{(2-42)}$$

$G^{E}{}_{P,T}$ is the excess Gibbs free energy.

By applying the Gibbs-Duhem relation to the equation (2-42) [36]:

$$n_{so} d(\ln(\hat{\gamma}_i)) + ns \sum_j \nu_j d(\ln(\hat{\gamma}_j)) = 0 \qquad \textbf{(2-43)}$$

The activity coefficient of component (i) is given as follows:

$$\ln\gamma_i = \frac{1}{RT}\left(\frac{\partial G_{P,T}{}^{E}}{\partial n_i} \right)_{n_j} \qquad \textbf{(2-44)}$$

2.2.4 Mean ionic activity coefficient

In electrolyte solutions, the activity of an electrolyte that dissociates into cation and anion in a solution cannot be estimated through evaluating the activity of one ionic species but through evaluating the activity of oppositely charged ions to ensure the electroneutrality condition. Considering a total dissociation of an electrolyte expressed by the following chemical equation:

$$C_{\nu_{C^+}}A_{\nu_{A^-}} \longrightarrow \nu_{c^+}C^+ + \nu_{A^-}A^- \qquad \textbf{(2-45)}$$

The chemical potential of electrolyte can be expressed as follows:

$$\mu_{C^+A^-} = \nu_{C^+}\mu_{C^+} + \nu_{A^-}\mu_{A^-} \qquad \textbf{(2-46)}$$

The chemical potential of cation can be expressed as follows:

$$\mu_{C^+} = \mu^*_{C^+} + RT\ln(x_{C^+}\gamma_{C^+}) \qquad \textbf{(2-47)}$$

The chemical potential of anion can be expressed as follows:

$$\mu_{A^-} = \mu^*_{A^-} + RT\ln(x_{A^-}\gamma_{A^-}) \qquad \textbf{(2-48)}$$

$\mu^*_{A^-}$ and $\mu^*_{c^+}$ are respectively the chemical potentials of anion and cation in the standard state based on the unsymmetrical convention and the mole fraction scale. γ_{A^-} and γ_{C^+} are respectively the activity coefficients of anion and cation based on the unsymmetrical convention and the mole fraction scale.

By inserting equations (2-47) and (2-48) into the equation (2-46):

$$\mu_{C^+A^-} = \mu^*_{C^+A^-} + RT\left[\nu_{C^+}\ln(x_{C^+}\gamma_{C^+}) + \nu_{A^-}\ln(x_{A^-}\gamma_{A^-})\right] \qquad \textbf{(2-49)}$$

By introducing the mean ionic mole fraction and the mean ionic activity coefficient concepts as shown in the equations (2-51) (b) and (2-51) (c):

$$\mu_{C^+A^-} = \mu^*_{C^+A^-} + \nu RT\ln\left(x_{CA^\pm}\gamma_{CA^\pm}\right) \qquad \textbf{(2-50)}$$

With ;

$$\left\{\begin{array}{ll} \mu^*_{C^+A^-} = \nu_{C^+}\mu^*_{C^+} + \nu_{A^-}\mu^*_{A^-} & \text{(a)} \\ x_{CA^\pm} = \left(x_{C^+}^{\nu_{C^+}}\, x_{A^-}^{\nu_{A^-}}\right)^{1/\nu} & \text{(b)} \\ \gamma_{CA^\pm} = \left(\gamma_{C^+}^{\nu_{c^+}}\gamma_{A^-}^{\nu_{A^-}}\right)^{1/V} & \text{(c)} \\ \nu = \nu_{C^+} + \nu_{A^-} & \text{(d)} \end{array}\right. \qquad \textbf{(2-51)}$$

$x_{CA^\pm}$ $\gamma_{CA^\pm}$ are the mean ionic mole fraction and the mean ionic activity coefficient of an electrolyte (CA), respectively.

2.2.5 Osmotic coefficient

The activities of water in electrolyte solutions are estimated by using the osmotic coefficient which is given by the following relation:

$$\ln(a_w) = -\frac{\varphi M_w \sum_j m_j}{1000} \qquad \textbf{(2-52)}$$

a_w, M_w and φ are the activity, the molecular weight and the osmotic coefficient of water, respectively. m_j is the molality of ion (j).

References

[1] Wilson, G. M. Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing. J. Am. Chem. Soc. 86, 127–130 (1964).

[2] Scheepers, J. J. Influence of temperature and intermolecular forces on volatile organic compounds-ester interactions (Doctoral dissertation, University of Johannesburg) (2012).

[3] Kontogeorgis, G. M.; Folas, G. K. Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories. John Wiley & Sons (2009).

[4] Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. AIChE J. 14, 135–144 (1968).

[5] Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems. AIChE J. 21, 116–128 (1975).

[6] Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. Group-contribution estimation of activity coefficients in nonideal liquid mixtures. AIChE J. 21, 1086–1099 (1975).

[7] Debye, P. V.; Hückel, E. Zur Theorie der Elektrolyte. Phys. Z, 24, 185 (1923).

[8] Guggenheim, EA; Fowler, RH, "Statistical thermodynamics," pp. 422ff, Cambridge Univ. Press. London (1949).

[9] Robinson, R. A.; Stokes, R. H. Electrolyte solutions. London, Butterworths Scientific Publications, 540-4 (1959).

[10] Bromley, L. A. Thermodynamic properties of strong electrolytes in aqueous solutions. AIChE J. 19, 313–320 (1973).

[11] Meissner, H. P.; Tester, J. W. Activity coefficients of strong electrolytes in aqueous solutions. Ind. Eng. Chem. Process Des. Dev. 11, 128–133 (1972).

[12] Pitzer, K. S. Thermodynamics of electrolytes. I. Theoretical basis and general equations. J. Phys. Chem. 77, 268–277 (1973).

[13] Pitzer, K. S.; Kim, J. J. Thermodynamics of Electrolytes.: IV. Activity and Osmotic Coefficients for Mixed Electrolytes. J. Am. Chem. Soc. 96, 5701 (1974).

[14] Pitzer, K. S. Electrolytes. from dilute solutions to fused salts. J. Am. Chem. Soc. 102, 2902–2906 (1980).

[15] Howard, J. J.; Pettitt, B. M. Integral equations in the study of polar and ionic interaction site fluids. J. Stat. Phys. 145, 441–466 (2011).

[16] Blum, L. Mean spherical model for asymmetric electrolytes. Mol. Phys. 30, 1529-1535 (1975).

[17] Cruz, J. L.; Renon, H. A new thermodynamic representation of binary electrolyte solutions nonideality in the whole range of concentrations. AIChE J. 24, 817-830 (1978).

[18] Chen, C. C.; Britt, H. I.; Boston, J. F.; Evans, L. B. Local composition model for excess Gibbs energy of electrolyte systems. AIChE J. 28, 588–596 (1982).

[19] Chen, C. C. ; Evans, L. B. A local composition model for the excess Gibbs energy of aqueous electrolyte systems. AIChE J. 32, 444 (1986).

[20] Papaiconomou, N.; Simonin, J.-P.; Bernard, O.; Kunz, W. MSA-NRTL model for the description of the thermodynamic properties of electrolyte solutions . Phys. Chem. Chem. Phys. 4, 4435-4443 (2002).

[21] Haghtalab, A.; Vera, J. H. A nonrandom factor model for the excess Gibbs energy of electrolyte solutions. AIChE J. 34, 803–813 (1988).

[22] Panayiotou, C.; Vera, J. H. The quasi-chemical approach for non-randomness in liquid mixtures. Expressions for local surfaces and local compositions with an application to polymer solutions. Fluid Phase Equilib. 5, 55–80 (1980).

[23] Meissner, H. P. Prediction of activity coefficients of strong electrolytes in aqueous systems. Thermodyn. Aqueous Syst. with Ind. Appl. 495–511 (1980).

[24] Zhao, E.; Yu, M.; Sauvé, R. E.; Khoshkbarchi, M. K. Extension of the Wilson model to electrolyte solutions. Fluid Phase Equilib. 173, 161–175 (2000).

[25] Xu, X.; Macedo, E. A. New Modified Wilson Model for Electrolyte Solutions. Ind. Eng. Chem. Res. 42, 5702–5707 (2003).

[26] Christensen, C.; Sander, B.; Fredenslund, A. A.; Rasmussen, P. Towards the extension of UNIFAC to mixtures with electrolytes. Fluid Phase Equilib. 13, 297–309 (1983).

[27] Sander, B.; Fredenslund, A.; Rasmussen, P. Calculation of vapour-liquid equilibria in mixed solvent/salt systems using an extended UNIQUAC equation. Chem. Eng. Sci. 41, 1171–1183 (1986).

[28] Nicolaisen, H.; Rasmussen, P.; Soerensen, J. M. Correlation and prediction of mineral solubilities in the reciprocal salt system (Na^+, K^+)(Cl^-, SO_4^{2-})-H_2O at 0-100°C. Chem. Eng. Sci. 48, 3149–3158 (1993).

[29] Sander, B. “Extended UNIFAC/UNIQUAC models for (1) gas solubilities and (2) electrolyte solutions,” Ph. D. Thesis, Dep. Chem. Eng. Tech. Univ. Denmark, DK-2800 Lyngby Denmark (1984).

[30] Haghtalab, A.; Mokhtarani, B. On extension of UNIQUAC-NRF model to study the phase behavior of aqueous two phase polymer-salt systems. Fluid Phase Equilib. 180, 139–149 (2001).

[31] Haghtalab, A.; Asadollahi, M. A. An excess Gibbs energy model to study the phase behavior of aqueous two-phase systems of polyethylene glycol+dextran. Fluid Phase Equilib. 171, 77–90 (2000).

[32] Kikic, I.; Fermeglia, M.; Rasmussen, P. Unifac prediction of vapor-liquid equilibria in mixed solvent-salt systems. Chem. Eng. Sci. 46, 2775–2780 (1991).

[33] Hansen, H. K.; Rasmussen, P.; Fredenslund, A.; Schiller, M.; Gmehling, J.

Vapor-liquid equilibria by UNIFAC group contribution. 5. Revision and extension. Ind. Eng. Chem. Res. 30, 2352-2355 (1991).

[34] Achard, C.; Dussap, C. G.; Gros, J. B. Representation of vapour-liquid equilibria in water-alcohol-electrolyte mixtures with a modified UNIFAC group-contribution method. Fluid Phase Equilib. 98, 71–89 (1994).

[35] Larsen, B. L.; Rasmussen, P.; Fredenslund, A. A Modified UNIFAC Group-Contribution Model for Prediction of Phase Equilibria and Heats of Mixing. Ind. Eng. Chem. Res. 26, 2274–2286 (1987).

[36] Thomsen, K. Aqueous electrolytes: model parameters and process simulation. Ph.D. Thesis (1997).

3. Model calculations

3.1 Introduction

The description of the phase behavior of multicomponent systems based on combining mathematical models with numerical methods provides a practical technique for solving phase equilibrium problems. A reliable thermodynamic treatment of electrolyte systems requires specifying various thermodynamic quantities to obtain complete phase equilibrium information of such systems. It is essential to develop methods for describing the distribution of different components involved in equilibrium separation processes. Such processes will split into layers at equilibrium with different compositions and it would be important to define specific equations to obtain equilibrium data for multicomponent electrolyte systems. Basically, thermodynamic models include parameters that must be adjusted using parameter estimation methods. These methods are generally based on the identification of an objective function to formalize properly the problem to be solved. This objective function is linked to an appropriate and efficient numerical method to estimate the unknown parameters. The regression of the thermodynamic model parameters is achieved by applying an optimization algorithm. The techniques referred here were based on the regression of the Extended UNIQUAC model parameters and the phase equilibrium calculations. Vapor-liquid flash calculations, as well as liquid-liquid flash calculations of multicomponent electrolyte systems, have been implemented on computer programs written in the FORTRAN language. In the following, the structure of the modeling framework achieved in this thesis will be presented.

3.2 Osmotic coefficient calculations

The partial dissociation of weak acids in aqueous solutions has been considered in this thesis work. This assumption led to represent the expression of the excess Gibbs energy as the sum of two contributions. The long-range contribution to the excess Gibbs energy is expressed by the term proposed by Fowler and Guggenheim. The short-range contribution to the excess Gibbs energy is represented by the traditional UNIQUAC equation. The consideration of partial dissociation in organic acid aqueous solutions involves the presence of other species that are in chemical equilibrium with each other. For an aqueous solution of a weak acid and water, the solution contains the solvent molecule (water), the undissociated electrolyte molecule and the ionic species. The distributions of species whose formations occur when electrolytes dissolve in water need evaluation of their activities in aqueous solutions. Consequently, it is preferable to conduct a calculation procedure for evaluating compositions of species of significant interest involved in aqueous solutions. In this work, this evaluation was designed for aqueous species of interest participating in the chemical equilibrium of interest. In other words, and based on the equilibrium constant values, species involved in the chemical equilibrium of high equilibrium constants, compared to those of other reactions, were selected as the main species in the aqueous solution and their insertions were considered in the modeling process. Also, presuming partial dissociation for weak acids implies further interactions between different species that are considered to be present in aqueous solutions.

The Extended UNIQUAC model was applied to five organic acid-water aqueous systems (see Chapter 4) to represent the osmotic coefficients of aqueous phosphoric acid solutions for the molality range from $0.1 \text{ to } 37\,(\text{mol/kg H}_2\text{O})$, of aqueous acetic acid solutions for the molality range from $0.3254 \text{ to } 14.9213\,(\text{mol/kg H}_2\text{O})$, of aqueous propionic acid solutions for the molality range from $0.3425 \text{ to } 12.4021\,(\text{mol/kg H}_2\text{O})$, of aqueous butyric acid solutions for the molality range from $0.2966 \text{ to } 17.5977\,(\text{mol/kg H}_2\text{O})$ and of aqueous formic acid solutions for the molality range from $0.3334 \text{ to } 5.6192\,(\text{mol/kg H}_2\text{O})$. Based on the values of equilibrium constants and based on the application of the model without increasing the number of adjustable parameters, the first dissociation equilibrium involved in organic acid-water aqueous systems was considered. Hence, the main aqueous species considered to be present in organic acids solutions include the undissociated form of organic acids, cations and anions resulting from the first chemical equilibrium. Another consideration was adopted in the application of the Extended UNIQUAC model to aqueous solutions and multicomponent aqueous-organic mixtures for which only the necessary interactions were taken into account in fitting model parameters. To allow easier application of the Extended UNIQUAC model in the representation of experimental data and beyond experimental data ranges, it was essential to assume that each anion is associated with each cation to take them as a single molecule in the calculation of thermodynamic properties. The interaction parameters of the Extended UNIQUAC model were adjusted based on Marquardt-Levenberg's optimization algorithm by minimizing the sum of squared differences between the experimental and the calculated osmotic coefficients. The optimal parameters were obtained with the determination of molalities while the first dissociation equilibrium of organic acids is considered. The equations used in the description of aqueous solutions of organic acids are given in Chapter 4.

The Marquardt-Levenberg algorithm is a popular numerical method widely used in nonlinear least-squares problems. The method is devoted to fit a parameterized function to a measured data set by minimizing the sum of the squares of the deviations between a given function and given experimental data points. The method aims to determine a vector of parameters of the regression of a function with respect to its unknown parameters so that the best fit with respect to model's parameters is obtained when the sum of the squared deviations between the experimental data and the data obtained by a model attains the minimum value. For a more detailed description of the Marquardt-Levenberg method, for example, refers to [1].

The manner in which the Extended UNIQUAC model was established based on an implementation of the Marquardt-Levenberg nonlinear least-squares method includes the following general attributes:

- Designation of model parameters subject to adjustments;
- In fitting the model parameters to experimental osmotic coefficients, the molalities were determined;
- The adjustment of six binary interaction parameters was intended to cover aqueous liquid compositions;
- The molalities of species contained in aqueous solutions of organic acids were determined and converted to mole fraction scale in the parameters optimization procedure;
- The osmotic coefficients were determined to calculate the chi-square function with respect to unknown parameters to seek of its convergence to a minimum acceptable.

3.3 Liquid-liquid equilibrium calculations

The description of equilibrium between two liquid phases specifying two-phase equilibrium properties in systems is characterized through equations related to the phase equilibrium condition. To solve a phase equilibrium problem, it is necessary to attribute a criteria relationship referring to the phase equilibrium. Defining the criteria for phase equilibrium must be considered in phase equilibrium calculations. When thermodynamic equilibrium is established between two liquid phases, the chemical potential (fugacity) of each component is the same in both phases. The equilibrium criteria of an aqueous-organic mixture based on the equality of chemical potential (fugacity) at constant pressure (P) and temperature (T) are given as follows:

$$\mu_i^{aq} = \mu_i^{org} \qquad \textbf{(3-1)}$$

$$f_i^{aq} = f_i^{org} \qquad \textbf{(3-2)}$$

Where μ_i^{aq} and μ_i^{org} are the chemical potentials in the aqueous and organic phases of component (i), respectively. f_i^{aq} and f_i^{org} are the fugacities in the aqueous and organic phases of component (i), respectively.

Further, the equilibrium condition defined in equation (3-2), in terms of fugacities, can be expressed in terms of activities or rewritten in terms of activity coefficients:

$$a_i^{aq} = a_i^{org} \qquad \textbf{(3-3)}$$

$$x_i^{aq}\gamma_i^{aq} = x_i^{org}\gamma_i^{org} \qquad \textbf{(3-4)}$$

with

$$a_i^{aq} = x_i^{aq}\gamma_i^{aq} \quad \text{and} \quad a_i^{org} = x_i^{org}\gamma_i^{org} \qquad \textbf{(3-5)}$$

a_i^{aq} and a_i^{org} are the activities in the aqueous and organic phases of component (i), respectively. γ_i^{aq} and γ_i^{org} are the activity coefficients in the aqueous and organic phases of component (i), respectively. x_i^{aq} and x_i^{org} are the mole fractions in the aqueous and organic phases of component (i), respectively.

Based on the equilibrium criteria between aqueous-organic mixtures given in equation (3-4), and by using the Extended UNIQUAC model, the calculation procedure of liquid-liquid equilibrium data for ternary and quaternary systems presented here was conducted by following this approach bounded with some restrictions. As will be emphasized in Chapters 4 and 5, phase equilibrium calculations were carried out to predict equilibrium compositions of two-phase systems from binary vapor-liquid and liquid-liquid equilibrium data used to determine binary model parameters for miscible and partially miscible binary subsystems, respectively. The undissociated and dissociated forms of weak electrolytes (assuming that each anion is paired with each cation) considered in aqueous solutions of organic acids were taken into account in parameter regressions. These parameters, the rest of unadjusted parameters from experimental data of either binary vapor-liquid or liquid-liquid equilibrium data, were fitted in liquid-liquid flash calculations to obtain the distribution of components between the two equilibrated liquid phases. In this context, different initial values were assigned to these parameters and remained fixed at these values to obtain a first estimate of aqueous and organic phase compositions. The obtained equilibrium compositions were then used for the regression of unknown parameters to ternary or quaternary equilibrium data using the objective function (equation (3-6)). Then, the adjusted parameters were used to obtain new liquid-liquid equilibrium data sets. This procedure was repeated until the phase equilibrium calculations converged to compositions and until the compositions proved to be physically acceptable.

$$H = \sum_{i=1}^{Ndata}\sum_{j=1}^{N}\left[x_j^{aq}\gamma_j^{aq}\left(x_j^{aq}, \underset{j\neq l}{\Delta u_{jl}}, \underset{l\neq j}{\Delta u_{lj}}\right) - x_j^{org}\gamma_j^{org}\left(x_j^{org}, \underset{j\neq l}{\Delta u_{jl}}, \underset{l\neq j}{\Delta u_{lj}}\right)\right]_i^2 \qquad \textbf{(3-6)}$$

N is the number of components and Ndata is the number of tie lines. Δu_{jl} and Δu_{lj} are binary interaction parameters between (j-l) and (l-j), respectively.

The formulation of the phase equilibrium calculation procedure for calculating liquid-liquid equilibrium data presented here was based on the approach described by Prausnitz et al. [2]. The liquid-liquid flash calculations used are described below.

A material balance on component (j) gives

$$Fz_j = L^{aq}x_j^{aq} + L^{org}x_j^{org} \qquad \textbf{(3-7)}$$

With,

$$F = L^{aq} + L^{org} \qquad \textbf{(3-8)}$$

Where F, L^{aq} and L^{org} are the flow rates of the feed, aqueous and organic phases, respectively. z_j is the feed mole fraction of component (j).

By considering the equation (3-8), the equation (3-7) yields:

$$z_j = x_j^{aq}\left(1 - \frac{L^{org}}{F}\right) + x_j^{org}\frac{L^{org}}{F} \qquad \textbf{(3-9)}$$

The equilibrium ratio of component (j) is given as follows:

$$k_j = \frac{x_j^{org}}{x_j^{aq}} \qquad \textbf{(3-10)}$$

The equation (3-9) is solved by considering that the mole fractions of the components in the two liquid phases are restricted by the following equation:

$$\sum_{j=1}^{N}\left(x_j^{org} - x_j^{aq}\right) = 0 \qquad \textbf{(3-11)}$$

Substitution of x_j^{org} from the equation (3-10) into the equation (3-9) yields:

$$z_j = x_j^{aq}(1-\alpha) + x_j^{aq}\,\alpha k_j \qquad \textbf{(3-12)}$$

With $\alpha = \frac{L^{org}}{F}$ the fraction of the feed that is split into the organic phase.

Substitution of the equation (3-12) into the equation (3-11) yields:

$$g(k_j, \alpha) = \sum_{j=1}^{N}\frac{z_j(K_j - 1)}{1 + \alpha(K_j - 1)} = 0$$

With, **(3-13)**

$$k_j = \frac{x_j^{org}}{x_j^{aq}} = \frac{\gamma_j^{aq}}{\gamma_j^{org}}$$

These equations are solved by a Globally Convergent Newton's method [3]. Phase equilibrium compositions were found by an iterative sequence. A first estimate was given to equilibrium ratios to permit the flash equilibrium calculations to launch. The values of equilibrium ratios are updated per iteration as well as the vector of functions to be solved. In some cases, the flash routine gave roots outside the valid composition range so that the physical meaning had to be considered to get roots that lie within the boundary range (i.e. $0 \prec x_j^{org} \prec 1$ and $0 \prec x_j^{aq} \prec 1$; and $\sum x_j^{org} = 1$ and $\sum x_j^{aq} = 1$,). Once the convergence criterion was attained, the flash routine terminates correctly to yield compositions covering the range of interest. As previously indicated, parameter regressions were carried out using the equation (3-6) and exploiting the output results obtained in liquid-liquid flash calculations related to equilibrium phase compositions.

3.4 Vapor-liquid equilibrium calculations

Isothermal and isobaric vapor-liquid equilibrium flash calculations for binary systems were performed. The calculation procedure used is similar to that described in the previous section. The principle requirement based on solving a set of equations to evaluate equilibrium properties between liquid phases applied to multicomponent systems was used for vapor-liquid equilibrium calculations for binary systems by considering the following equations:

The equilibrium criteria between the liquid and vapor phases:

$$f_j^L = f_j^V \tag{3-14}$$

$$f_j^L = \gamma_j x_j \varphi_j^S P_j^S$$

(3-15)

$$f_j^V = \varphi_j^V y_j P$$

φ_j^V is the fugacity coefficient of component (j) in the vapor phase. φ_j^S is the fugacity coefficient of pure component (j) in its saturated state. The ratio $\frac{\varphi_j^V}{\varphi_j^s}$ can be set equal to unity for low pressure. P is the total pressure in the system. P_j^S is the vapor pressure of component (j) at system temperature. y_j and x_j are the mole fractions in the vapor and liquid phases of component (j), respectively. Here α denotes the fractional vaporization.

$$g(k_j, \alpha) = \sum_{j=1}^{N} \frac{z_j(K_j - 1)}{1 + \alpha(K_j - 1)} = 0$$

With, **(3-16)**

$$k_j = \frac{y_j}{x_j} = \frac{\gamma_j P_j^S}{P}$$

References

[1] Moré, J. J. The Levenberg-Marquardt algorithm: implementation and theory. Numerical Analysis. Springer, Berlin, Heidelberg. 630, 105-116. (1978).

[2] Prausnitz, J. M.; Anderson, F. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R.; O'connell, J. P. Computer calculations for multicomponent vapor-liquid and liquid-liquid equilibria. Englewood Cliffs, NJ: Prentice-Hall. 120 (1980).

[3] Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. Numerical recipes in C++.The art of scientific computing. 2, 1002 (2007).

4. The inclusion of organic acids dissociation in the prediction of ternary liquid-liquid equilibrium (LLE) data

4.1 Introduction

The presences of the electrolytes in aqueous solutions have a particular role in industrial processes of chemical engineering, particularly in separation processes (extraction, distillation). The peculiarity of the chosen systems can be described according to which a solute can partially dissociate, in this case, an aqueous solution contains himself the ionic species resulting from the dissociation of solute, the molecule of the undissociated solute and the molecule of solvent (water).

The prediction or correlation of liquid-liquid equilibrium data of various systems has aroused the interest of several research works. Several works have been reported in the literature, either by experimental methods or by numerical methods represented by excess Gibbs energy models (NRTL, UNIQUAC, UNIFAC etc) on the liquid-liquid extraction of carboxylic acids and phosphoric acid. The common objective of these works was to see the extraction power of organic solvents used (alcohols, ethers, amines etc) with respect to the extraction of these organic acids from aqueous solutions [1–12]. The authors of the works mentioned above did not consider that these organic components dissociate in water. It is therefore reasonable to think that these organic acids dissociate in water causing ionic species in the solution. Therefore, it is necessary to include their dissociation in the calculation of the thermodynamic equilibrium. The computation of phase equilibrium of a system containing an electrolyte resulting from the dissociation of an organic acid is complex, this complexity will increase by the number of adjusted parameters, that on the one hand, and in other word in the case where the liquid-liquid equilibrium data are predicted from binary data. Indeed, the consideration of the dissociation of an organic acid can rigorously influence the equilibrium phase compositions.

The liquid-liquid equilibrium study of electrolyte solutions has a practical interest at the industrial level. In addition, experimental liquid-liquid equilibrium data of electrolyte solutions are not always available, hence the need to model and predict the thermodynamic properties through precise models that account for all interactions between molecular and ionic species.

The objective of this work is to consider the dissociation of carboxylic acids (i.e. acetic, formic, propionic and butyric acids) and phosphoric acid by comparing the influence of this consideration on the equilibrium phase compositions with respect to authors [6, 7, 12] who did not include, it on the one side, and the other to study the capacity of the Extended UNIQUAC model to predict the liquid-liquid equilibrium data of chosen systems from binary data. They are all type I systems, where two binaries are completely miscible and the third binary is partially miscible. Two types of data sources are distinguished, the interaction parameters for the completely miscible binaries are adjusted using the vapor–liquid equilibrium data if they exist and the liquid-liquid equilibrium (mutual solubility) data are used in order to determine the interaction parameters for the partially miscible binary. The Extended UNIQUAC model has been applied for five systems: water-phosphoric acid-methylisobutylketone-(H^+,$H_2PO_4^-$), water-acetic acid-cumene-(H^+,CH_3COO^-), water-propionic acid-cumene-(H^+,$CH_3CH_2COO^-$), water-formic acid-isoamyl acetate-(H^+,$HCOO^-$) and water-butyric acid-isoamyl acetate-(H^+,$CH_3CH_2CH_2COO^-$) at T=298.15K.

4.2 Thermodynamic modeling

4.2.1 The basis of the calculation of the liquid-liquid equilibrium

The activity coefficient and the mole fraction are the grandeurs necessary to describe the liquid-liquid equilibrium, where they are expressed by the following equation:

$$\begin{cases} x_i^{aq}\gamma_i^{aq} = x_i^{org}\gamma_i^{org} \\ \sum\limits_{i=1}^{N} x_i^{aq} = 1 \qquad i = 1, N \\ \sum\limits_{i=1}^{N} x_i^{org} = 1 \end{cases} \tag{4-1}$$

Where N is the number of the Components, x_i^{aq} and x_i^{org} are respectively the mole fractions in the aqueous phase and in the organic phase of component (i). γ_i^{aq} and γ_i^{org} are respectively the activity coefficients in the aqueous phase and in the organic phase of component (i).

In the case of a mixture including an electrolyte, the liquid-liquid equilibrium of an electrolyte (j) is described by the equation (4-2):

$$\begin{cases} x_{ca\pm j}^{aq}\gamma_{ca\pm j}^{aq} = x_{ca\pm j}^{org}\gamma_{ca\pm j}^{org} \end{cases} \tag{4-2}$$

$\gamma_{ca\pm j}^{aq}$ and $\gamma_{ca\pm j}^{org}$ are the mean ionic activity coefficients of an electrolyte (j) in the aqueous phase and in the organic phase, respectively. The mean ionic activity coefficient of an electrolyte (j) is defined as follow:

$$\gamma_{ca\pm j} = (\gamma_{c+}^{\upsilon_{c+}} \times \gamma_{a-}^{\upsilon_{a-}})^{\left(\frac{1}{\upsilon_{c+}+\upsilon_{a-}}\right)} \tag{4-3}$$

Where υ_{c+} and υ_{a-} are respectively the stoichiometric coefficients for the cation and for the anion. $x^{aq}_{ca\pm j}$ and $x^{org}_{ca\pm j}$ are respectively the mean ionic mole fractions of an electrolyte (j) in the aqueous phase and in the organic phase. These quantities are calculated in the same manner as shown in equation (4-3).

4.2.2 The thermodynamic model

In this work, we use the model proposed by Nicolaisen et al. [13], extended version to the electrolytes solutions. The model is based on the concept of local compositions proposed by Abrams and Prausnitz [14], Maurer and Prausnitz [15], this original version of the UNIQUAC model is extended by the addition of the Debye-Hückel term [16,17]. The excess Gibbs energy (G^E) (equation (4-4)) is composed of three terms: an electrostatic term, a combinatorial term (entropic) and a residual term (enthalpic). The expression of the excess Gibbs energy of combinatorial and residual terms that take into account the short range forces are identicals to those used in original UNIQUAC model. The combinatorial term is given in the equation (4-5).

$$\frac{G^E}{RT}=\frac{G^E_{D-H}}{RT}+\frac{G^E_{Com}}{RT}+\frac{G^E_{Res}}{RT} \quad \textbf{(4-4)}$$

$$\frac{G^E_{Com}}{RT}=\sum_i x_i \ln\left(\frac{\varphi_i}{x_i}\right)-\frac{Z}{2}\sum_i x_i q_i \ln\left(\frac{\varphi_i}{\theta_i}\right) \quad \textbf{(4-5)}$$

Z=10 is the co-ordination number, x_i is the mole fraction, φ_i and θ_i are respectively volume and surface area fractions of component (i).

$$\varphi_i=\frac{r_i x_i}{\sum_k r_k x_k} \qquad \theta_i=\frac{q_i x_i}{\sum_k q_k x_k} \quad \textbf{(4-6)}$$

r_i and q_i are respectively volume and surface area parameters of component (i). The residual term is given as follows:

$$\frac{G^E_{Res}}{RT}=-\sum_i x_i q_i \ln\left(\sum_j \theta_j \psi_{ji}\right) \quad \textbf{(4-7)}$$

The interaction parameter ψ_{ji} is given by:

$$\psi_{ji}=\exp\left(-\frac{\Delta u_{ji}}{RT}\right) \quad \textbf{(4-8)}$$

T is the absolute temperature and R is the ideal gas constant. Δu_{ji} is the binary interaction parameters.

The Debye-Hückel [18] term which represents the interactions between ions, long range forces, is given as follows:

$$\frac{G^{E}_{D-H}}{RT} = -x_W M_W \frac{4A}{b^3}\left[\ln(1+b\sqrt{I}) - b\sqrt{I} + \frac{b^2 I}{2}\right] \quad \textbf{(4-9)}$$

$$A = \begin{bmatrix} 1.131 + 1.335*10^{-3}*(T-273.15) \\ +1.164*10^{-5}*(T-273.15)^2 \end{bmatrix} kg^{1/2}\ mol^{-1/2} \quad \textbf{(4-10)}$$

Where, x_w is the mole fraction of water, M_W is the molecular weight of water, $b = 1.5\,(Kg\ mol^{-1})^{1/2}$ is a constant. A is the Debye-Hückel parameter defined in equation (4-10) and I is the ionic strength is given by:

$$I = \frac{1}{2}\sum_j z_j^2 m_j \quad \textbf{(4-11)}$$

m_j is the molality and z_j is the charge of ion (j).

The activity coefficient of the Debye-Hückel term is obtained by partial molal differentiation of the equation (4-9). The activity coefficient of an ionic species (j) is:

$$\ln\gamma_j^{D-H} = -z_j^2 \frac{A\sqrt{I}}{1+b\sqrt{I}} \quad \textbf{(4-12)}$$

The activity coefficient of water is:

$$\ln\gamma_W^{D-H} = M_W \frac{2A}{b^3}\left[1 + b\sqrt{I} - \frac{1}{1+b\sqrt{I}} - 2\ln(1+b\sqrt{I})\right] \quad \textbf{(4-13)}$$

The activity coefficients of the combinatorial and residual terms are obtained by partial molal differentiation of the equations (4-5) and (4-7). The symmetrical activity coefficient of combinatorial term of component (i) is:

$$\ln\gamma_i^{Com} = \ln\left(\frac{\varphi_i}{x_i}\right) - \frac{\varphi_i}{x_i} + 1 - \frac{Z}{2} q_i\left[\ln\left(\frac{\varphi_i}{\theta_i}\right) - \frac{\varphi_i}{\theta_i} + 1\right] \quad \textbf{(4-14)}$$

The symmetrical activity coefficient of residual term of component (i) is:

$$\ln\gamma_i^{Res} = q_i\left[1 - \ln\left(\sum_j \theta_j \psi_{ji}\right) - \sum_j \frac{\theta_j \psi_{ij}}{\sum_l \theta_l \psi_{lj}}\right] \quad \textbf{(4-15)}$$

Equations (4-14) and (4-15) must be normalized at infinite dilution by setting $x_w = 1$.

The unsymmetrical activity coefficient of combinatorial term of component (i) is:

$$\ln\gamma_i^{\infty,Com} = \ln\left(\frac{r_i}{r_W}\right) - \frac{r_i}{r_W} + 1 - \frac{Z}{2} q_i\left[\ln\left(\frac{r_i q_W}{r_W q_i}\right) - \frac{r_i q_W}{r_W q_i} + 1\right] \quad \textbf{(4-16)}$$

The unsymmetrical activity coefficient of residual term of component (i) is:

$$\ln\gamma_i^{\infty,\mathrm{Res}} = q_i\left[1-\ln\left(\psi_{wi}\right)-\psi_{iw}\right] \tag{4-17}$$

The activity coefficient of a solvent molecule (water) (k) is obtained by the addition of the three terms:

$$\ln\gamma_k = \ln\gamma_k^{\mathrm{D-H}} + \ln\gamma_k^{\mathrm{Com}} + \ln\gamma_k^{\mathrm{Res}} \tag{4-18}$$

The activity coefficient of ionic species (j) is obtained by the addition of these terms:

$$\ln\gamma_j = \ln\gamma_j^{\mathrm{D-H}} + \ln\gamma_j^{\mathrm{Com}} - \ln\gamma_j^{\infty,\mathrm{Com}} + \ln\gamma_j^{\mathrm{Res}} - \ln\gamma_j^{\infty,\mathrm{Res}} \tag{4-19}$$

The volume and surface area parameters for ionic species and for organic acids are obtained from Christensen and Thomsen [19], Yan et al. [20], Laleh Seyed Saadat et al. [8], and those of water and organic solvents were taken from Anderson and Prausnitz [21], Mafra el al. [22] and Gilani et al. [6]. Table 4.1 tabulates the values of the volume and surface area parameters of components. Table 4.2 presents the dissociation constants of organic acids treated in this work. The model is normalized to infinite dilution by granting unsymmetrical convention for the ions and for solutes. We have considered that each anion is associated with cation to take them as a molecule. We have chosen the infinite dilution in water as a reference state for both phases.

4.3 Results and discussion

4.3.1 Procedure for estimating parameters

As we mentioned previously, the aim of this work is to include the dissociation of the chosen organic acids in the process of phase equilibrium calculations based on data from the literature according to the type of subsystem envisaged. The evaluation of the parameters of the model requires experimental data of various types. We have opted to divide the studied systems into subsystems to study the phase equilibrium and obtain the thermodynamic properties of the systems: water-phosphoric acid-MIBK-(H^+,$H_2PO_4^-$), water-acetic acid-cumene-(H^+,CH_3COO^-), water-propionic acid-cumene-(H^+,$CH_3CH_2COO^-$), water-formic acid-isoamyl acetate-(H^+,$HCOO^-$) and water-butyric acid-isoamyl acetate-(H^+,$CH_3CH_2CH_2COO^-$).

The concerned systems are all type I systems, which have a plait point, the approaches have been considered to estimate the parameters of the Extended UNIQUAC model. The liquid-liquid equilibrium data have been used for the partially miscible subsystems: H_2O(1)-MIBK(3), H_2O(1)-C_9H_{12}(3) and H_2O(1)-$C_7H_{14}O_2$(3), the equality of the activity coefficients of each component in the two liquid phases has been resolved by the numerical method in [23] to find the interaction parameters of these types of subsystems.

The vapor-liquid equilibrium data have been used for the completely miscible subsystems: H_2O(1)-H_3PO_4(2)-(H^+,$H_2PO_4^-$)(4), H_2O(1)-CH_3COOH(2)-(H^+,CH_3COO^-)(4), H_2O(1)-CH_3CH_2COOH(2)-(H^+,$CH_3CH_2COO^-$)(4), H_2O(1)-$HCOOH$(2)-(H^+,$HCOO^-$)(4)

and H_2O(1)-$CH_3CH_2CH_2COOH$(2)-(H^+,$CH_3CH_2CH_2COO^-$)(4). The optimization of these parameters was carried out by minimizing the sum of squared differences between the experimental and calculated values using the algorithm in [24]. The rest of parameters between: H_3PO_4(2)-MIBK(3)-(H^+,$H_2PO_4^-$)(4), CH_3COOH(2)-C_9H_{12}(3)-(H^+,CH_3COO^-)(4), CH_3CH_2COOH(2)-C_9H_{12}(3)-(H^+,$CH_3CH_2COO^-$)(4), HCOOH(2)-$C_7H_{14}O_2$(3)-(H^+,$HCOO^-$)(4) and $CH_3CH_2CH_2COOH$(2)-$C_7H_{14}O_2$(3)-(H^+,$CH_3CH_2CH_2COO^-$)(4) were found in the prediction of the liquid-liquid equilibrium data using the parameters obtained by the methods mentioned above. In the next sections, we will describe the calculation methods used for each subsystem.

4.3.2 Modeling vapor-liquid equilibrium

4.3.2.1 The subsystem H_2O(1)-H_3PO_4(2)-(H^+,$H_2PO_4^-$)(4)

Several studies have been carried out for correlating the thermodynamic properties of the system H_3PO_4-H_2O. Pitzer and Silvester [25] have described the osmotic coefficient in aqueous solutions of phosphoric acid for a molality of 6 M. They have taken into account only the first dissociation of the phosphoric acid which is written as follows:

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \qquad \textbf{(4-20)}$$

Stig et al. [26] have applied Bromley model [27] to calculate the activity coefficients and the activity of the phosphoric acid was expressed as a polynomial of ionic strength. They have put into play all equations corresponding to the dissociation of the phosphoric acid in the aqueous phase for a concentration varies from 0.02 to 6.7 M of phosphoric acid.

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \qquad \textbf{(4-20)}$$

$$H^+ + 2H_2PO_4^- \rightleftharpoons H_5P_2O_8^- \qquad \textbf{(4-21)}$$

$$2H_2PO_4^- + 2H^+ \rightleftharpoons H_6P_2O_8 \qquad \textbf{(4-22)}$$

Christensen and Thomsen [19] have used the Extended UNIQUAC model to study the system H_3PO_4-H_2O, the model showed a validity of 12 mol/kg of phosphoric acid. They have added to the equation (4-20), the equation (4-23) to apply their study:

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad \textbf{(4-23)}$$

Table 4.1: Volume and surface area parameters

Components	r	q	References
H_2O	0.92	1.40	[21]
H_3PO_4	1.69	3.46	[19]
$C_6H_{12}O$	4.60	4.03	[21]
$H_2PO_4^-$	8.30	8.19	[19]
H^+	1	1	[20]
C_9H_{12}	5.04	3.81	[22]
CH_3COOH	2.20	2.07	[8]
CH_3COO^-	2.05	1.90	[20]
CH_3CH_2COOH	2.88	2.61	[8]
$CH_3CH_2COO^-$	2.05	1.90	[20]
$C_7H_{14}O_2$	5.27	4.49	[6]
HCOOH	1.53	1.53	[8]
$HCOO^-$	2.05	1.90	[20]
$CH_3CH_2CH_2COOH$	3.55	3.15	[8]
$CH_3CH_2CH_2COO^-$	2.05	1.90	[20]

In this subsystem, six interaction parameters were adjusted. Since the second and third equilibrium constant are lower than the first one, we take into account just the first dissociation of the phosphoric acid described by equation (4-20) . In the modeling process, the determined molalities of the species contained in an aqueous phosphoric acid solution are converted on mole fraction scale.

Table 4.2: Dissociation constants of organic acids

Organic acids	Chemical formula	k	References
Phosphoric acid	H_3PO_4	0.007107	[29]
Acetic acid	CH_3COOH	0.0000175	[30]
Propionic acid	CH_3CH_2COOH	0.0000133	[30]
Formic acid	HCOOH	0.000177	[30]
Butyric acid	$CH_3CH_2CH_2COOH$	0.0000152	[30]

The calculations of molalities consist to solve a nonlinear system of equations describing the mass balance of the phosphoric acid, the equilibrium constant of the first dissociation of the phosphoric acid and the condition of the electroneutrality:

$$\begin{cases} \bar{m} = m_{AC} + m_{A-} \\ k = \dfrac{m_{C+} \times m_{A-}}{m_{AC}} \times \dfrac{\gamma_{C+} \times \gamma_{A-}}{\gamma_{AC}} \\ m_{C+} = m_{A-} \end{cases} \qquad \textbf{(4-24)}$$

Where AC is H_3PO_4, C^+ is H^+ and A^- is $H_2PO_4^-$.The experimental data reported by Elmore et al. [28] were used to calculate the osmotic coefficient expressed in equation (4-26) for a molality range varies from 0.1 to 37 mol/kg of phosphoric acid. The correlation of the osmotic coefficient requires six interaction parameters of this subsystem that contains a single electrolyte and two molecules. The minimization was carried out by the numerical method in [24], the sum of squared differences between the experimental and the calculated values corresponding to the osmotic coefficients of the following objective function:

$$F(P)=\sum_{i=1}^{N}\left[\left(\frac{\varphi^{cal}(P)-\varphi^{exp}}{\varphi^{exp}}\right)^{2}_{i}\right] \qquad \textbf{(4-25)}$$

The osmotic coefficient is given by the following relation:

$$\varphi=-\frac{1000}{M_W \upsilon \overline{m}}\ln(a_W) \qquad \textbf{(4-26)}$$

a_w, M_w, υ and $\overline{m}$ are the water activity, the molecular weight of water, the Stoichiometric coefficient and the mass balance of H_3PO_4, respectively. $\upsilon=2$ .The results of the correlation are shown in Figure 4.1 and illustrated in Table 4.3 as well as the interaction parameters are shown in Table 4.4.

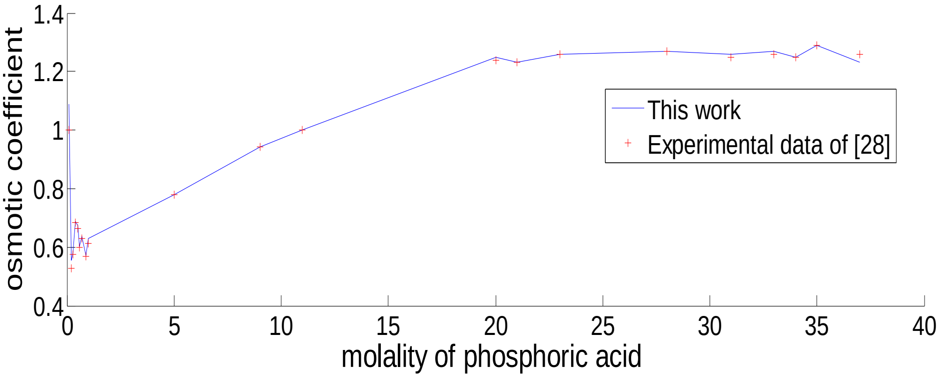

Figure 4.1: Osmotic coefficient in function of molality in aqueous solutions of phosphoric acid at 298.15 K

4.3.2.2 The subsystems of carboxylic acids

The calculation procedure described in the previous section is applied to model the following subsystems: $H_2O(1)$-$CH_3COOH(2)$-(H^+,CH_3COO^-)(4), $H_2O(1)$-$CH_3CH_2COOH(2)$-(H^+,$CH_3CH_2COO^-$)(4), $H_2O(1)$-$HCOOH(2)$-(H^+,$HCOO^-$)(4) and $H_2O(1)$-$CH_3CH_2CH_2COOH(2)$-(H^+,$CH_3CH_2CH_2COO^-$)(4). The first dissociation of carboxylic (i.e. acetic, propionic, formic and butyric) acids was included in the modeling of vapor-liquid equilibrium. Six interaction parameters were adjusted for per subsystem of the subsystems mentioned above.

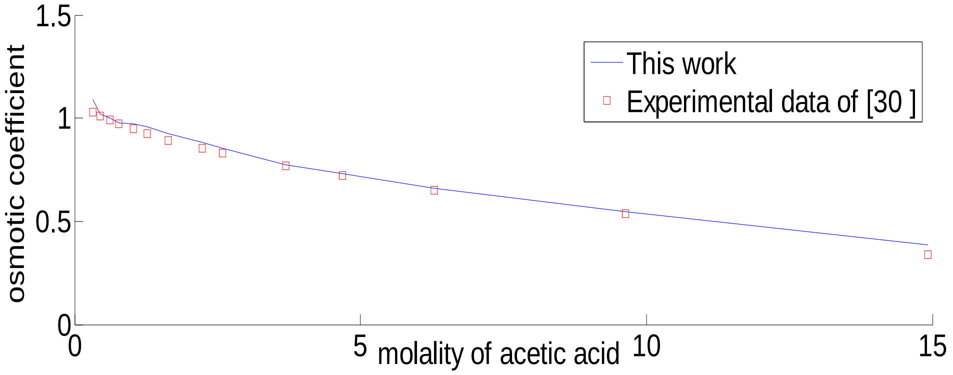

Figure 4.2: Osmotic coefficient in function of molality in aqueous solutions of acetic acid at 298.15 K

The objective function (4-25) is minimized by the sum of squared differences between experimental data in [30] and the calculated values by the Extended UNIQUAC model. The results of the correlation are illustrated in Figures 4.2-5. The standard deviations between the calculated and the experimental osmotic coefficients are tabulated in Table 4.3. The interaction parameters of these subsystems are listed in Table 4.4.

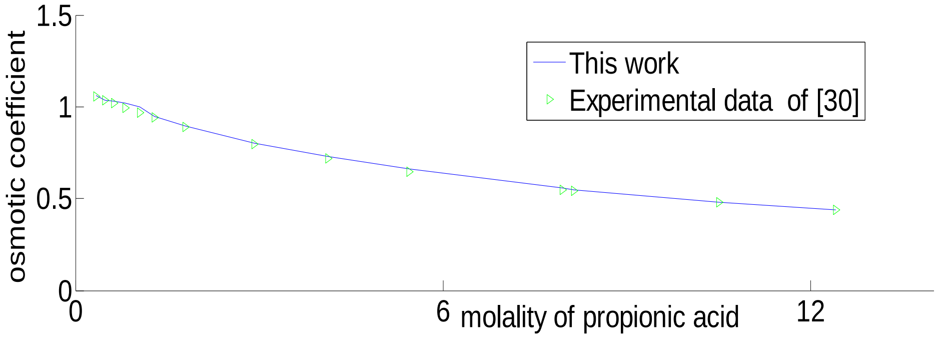

Figure 4.3: Osmotic coefficient in function of molality in aqueous solutions of propionic acid at 298.15 K

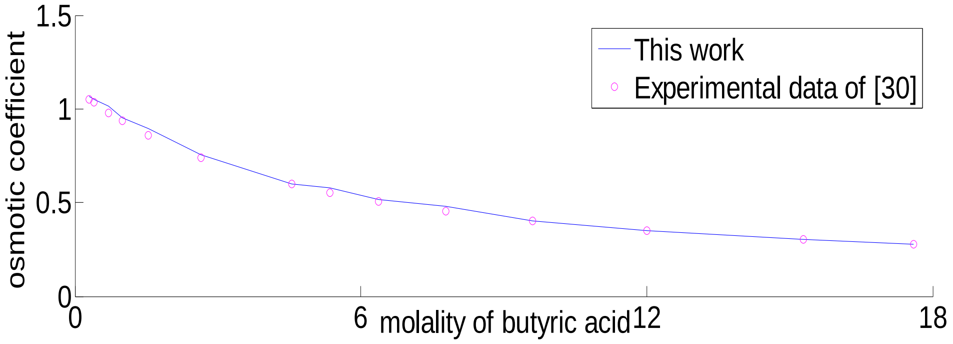

Figure 4.4: Osmotic coefficient in function of molality in aqueous solutions of butyric acid at 298.15 K

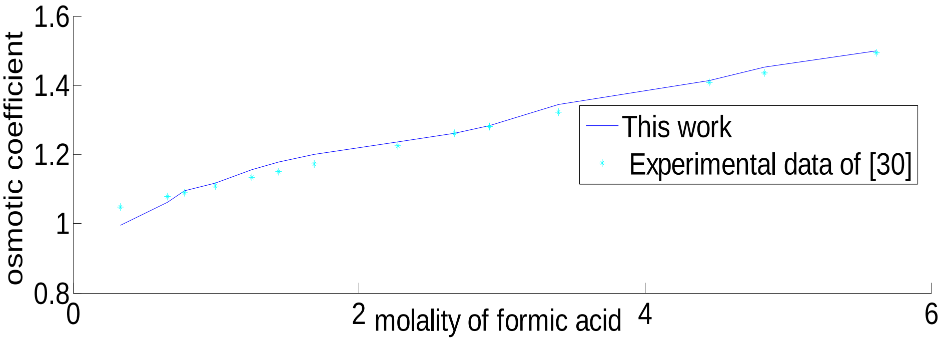

Figure 4.5: Osmotic coefficient in function of molality in aqueous solutions of formic acid at 298.15 K

4.3.3 The partially miscible subsystems

The experimental data published in [6, 7, 12] relating to the mutual solubility between H_2O(1)-MIBK(3), H_2O(1)-C_9H_{12}(3) and H_2O(1)-$C_7H_{14}O_2$(3) are used to adjust the interaction parameters by solving the system of equation (4-27). The resolution of this system is performed by the iterative method described in [23]. The obtained parameters are given in Table 4.4.

$$G = \sum_i (x_i\gamma_i)^{aq} - (x_i\gamma_i)^{org} \qquad \textbf{(4-27)}$$

4.3.4 Prediction of liquid-liquid equilibrium

The obtained parameters by the methods mentioned in the preceding sections are exploited to find the parameters of these subsystems: H_3PO_4(2)-MIBK(3)-(H^+,$H_2PO_4^-$)(4), CH_3COOH(2)-C_9H_{12}(3)-(H^+,CH_3COO^-)(4), CH_3CH_2COOH(2)-C_9H_{12}(3)-(H^+,$CH_3CH_2COO^-$)(4), $HCOOH$(2)-$C_7H_{14}O_2$(3)-(H^+,$HCOO^-$)(4) and $CH_3CH_2CH_2COOH$(2)-$C_7H_{14}O_2$(3)-(H^+,$CH_3CH_2CH_2COO^-$)(4). These parameters are optimized by solving a system of equations based on two criteria: the minimization of an objective function and the calculation of the liquid-liquid equilibrium data by the Extended UNIQUAC model.

These two criteria are translated by the system of equations (4-28). Where, N is the number of components and Ndata is the number of tie lines. The resolution of (4-28) was carried out by the algorithm in [24]. The standard error between the mass fractions experimental and those calculated is measured by Root-Mean Square Deviation (RMSD) according to the equation (4-29).

$$\begin{cases} H = \sum_{i=1}^{Ndata} \sum_{j=1}^{N} \left[(x_j \gamma_j)^{aq} - (x_j \gamma_j)^{org} \right]_i^2 \\ \sum_{j=1}^{N} x_j^{aq} = 1 \\ \sum_{j=1}^{N} x_j^{org} = 1 \end{cases} \tag{4-28}$$

$$RMSD = \sqrt{\frac{\sum_{i=1}^{Ndata} \sum_{j=1}^{N} (x_{ji}^{aq,exp} - x_{ji}^{aq,cal})^2 + (x_{ji}^{org,exp} - x_{ji}^{org,cal})^2}{6 * Ndata}} \tag{4-29}$$

Table 4.4 shows the interaction parameters for the studied systems and the deviations between the calculated mass fractions by including the first dissociation of organic acids in the phase equilibrium modeling and the experimental mass fractions. The Figures 4.6-10 illustrated a comparison between the experimental tie lines in [6, 7, 12] and those predicted from binary data by including the first dissociation of organic acids in the modeling process. According to the Figure 4.6, the solubility of the phosphoric acid increases in both phases, in particular in the aqueous phase. It can be noted that the mass fractions of the phosphoric acid in the organic phase predicted by the model are important especially at initial low concentrations of phosphoric acid but this behavior is attenuated at its initial high concentrations.

The results presented in Figure 4.7 and Figure 4.8 for the systems: $H_2O(1)$-$CH_3COOH(2)$-$C_9H_{12}(3)$ and $H_2O(1)$-$HCOOH(2)$-$C_7H_{14}O_2(3)$, have shown that acetic and formic acids tend to remain in the aqueous phase. This can be interpreted by the fact that the predicted mass fractions of these two organic acids in the organic phase are much lower than those of the preceding example and their mass fractions increase rapidly in the aqueous phase, in particular for acetic acid.

Unlike the preceding examples, propionic and butyric acids have recognized that their mass fractions in the organic phase are much greater than those in the aqueous phase. The model predicts a large concentration of solute that has migrated outside the aqueous phase for systems: $H_2O(1)$-$CH_3CH_2COOH(2)$-$C_9H_{12}(3)$ and $H_2O(1)$-$CH_3CH_2CH_2COOH(2)$-$C_7H_{14}O_2(3)$. The Figure 4.9 shows that the tie lines appear better than those illustrated in Figure 4.10.

Table 4.3: Standard deviations between experimental and calculated values of osmotic coefficients at 298.15 K

Subsystems	Molality ranges	Number of data points	Standard deviations
$H_2O(1)-H_3PO_4(2)-(H^+,H_2PO_4^-)(4)$	0.1-37	21	0.0231
$H_2O(1)-CH_3COOH(2)-(H^+,CH_3COO^-)(4)$	0.3254-14.9213	14	0.0268
$H_2O(1)-CH_3CH_2COOH(2)-(H^+,CH_3CH_2COO^-)(4)$	0.3425-12.4021	14	0.0123
$H_2O(1)-HCOOH(2)-(H^+,HCOO^-)(4)$	0.3334-5.6192	14	0.0204
$H_2O(1)-CH_3CH_2CH_2COOH(2)-(H^+,CH_3CH_2CH_2COO^-)(4)$	0.2966-17.5977	14	0.0181

Table 4.4: UNIQUAC binary interaction parameters

Systems	Temperature (K)	System type	UNIQUAC binary interaction parameters												RMSD
System 1	298.15	I	Δu_{14}	Δu_{41}	Δu_{12}	Δu_{21}	Δu_{24}	Δu_{42}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}	Δu_{34}	Δu_{43}	0.0761
$H_2O(1)-H_3PO_4(2)-MIBK(3)-(H^+, H_2PO_4^-)(4)$			0.958	1.50	1.57	2.30	1.96	1.85	–0.190	8.82	259.88	-166.28	-212.19	-47.97	
System 2	298.15	I	Δu_{14}	Δu_{41}	Δu_{12}	Δu_{21}	Δu_{24}	Δu_{42}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}	Δu_{34}	Δu_{43}	0.0549
$H_2O(1)-CH_3COOH(2)-C_9H_{12}(3)-(H^+, CH_3COO^-)(4)$			34.66	25.43	16.55	1.93	11.50	6.60	0.0270	48.83	-57.49	-44.55	137.24	-79.81	
System 3	298.15	I	Δu_{14}	Δu_{41}	Δu_{12}	Δu_{21}	Δu_{24}	Δu_{42}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}	Δu_{34}	Δu_{43}	0.0596
$H_2O(1)-CH_3CH_2COOH(2)-C_9H_{12}(3)-(H^+, CH_3CH_2COO^-)(4)$			36.91	27.36	18.34	3.30	13.18	8.17	0.0441	91.42	180.97	-92.93	36.59	- 217.61	
System 4	298.15	I	Δu_{14}	Δu_{41}	Δu_{12}	Δu_{21}	Δu_{24}	Δu_{42}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}	Δu_{34}	Δu_{43}	0.0493
$H_2O(1)-HCOOH(2)-C_7H_{14}O_2(3)-(H^+, HCOO^-)(4)$			46.46	36.12	26.53	10.10	20.61	15.11	–0.307	11.26	-416.90	-10.11	-1250	82.86	
System 5	298.15	I	Δu_{14}	Δu_{41}	Δu_{12}	Δu_{21}	Δu_{24}	Δu_{42}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}	Δu_{34}	Δu_{43}	0.0938
$H_2O(1)-CH_3CH_2CH_2COOH(2)-C_7H_{14}O_2(3)-(H^+, CH_3CH_2CH_2COO^-)(4)$			39.91	29.86	20.33	5.11	15.11	10.04	–0.0554	25.35	40.16	-14.27	-1254.01	1213.91	

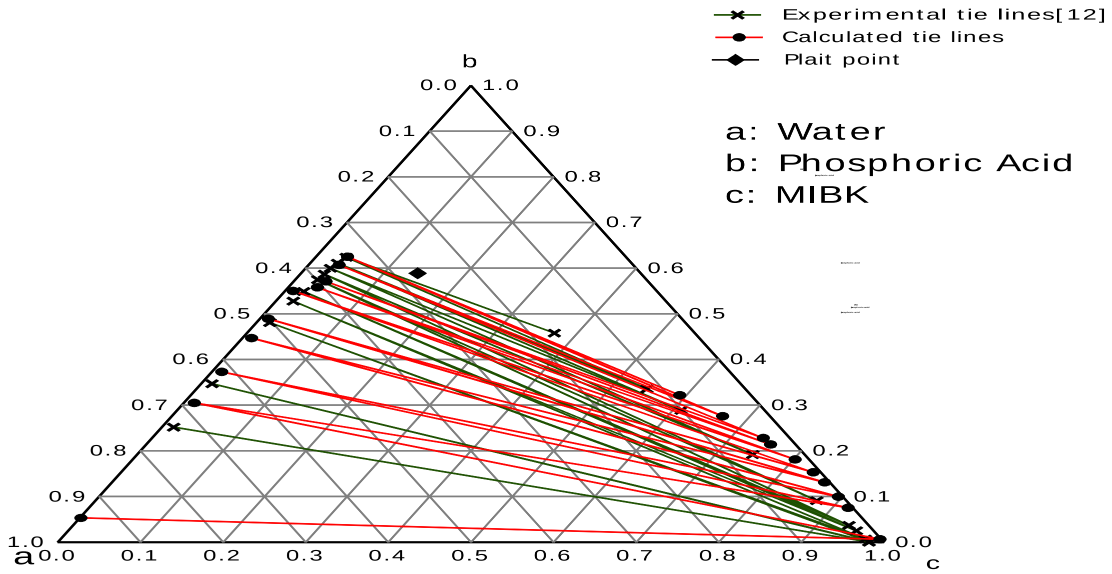

Figure 4.6: Liquid-liquid equilibrium data for system water-phosphoric acid-MIBK at 298.15 K

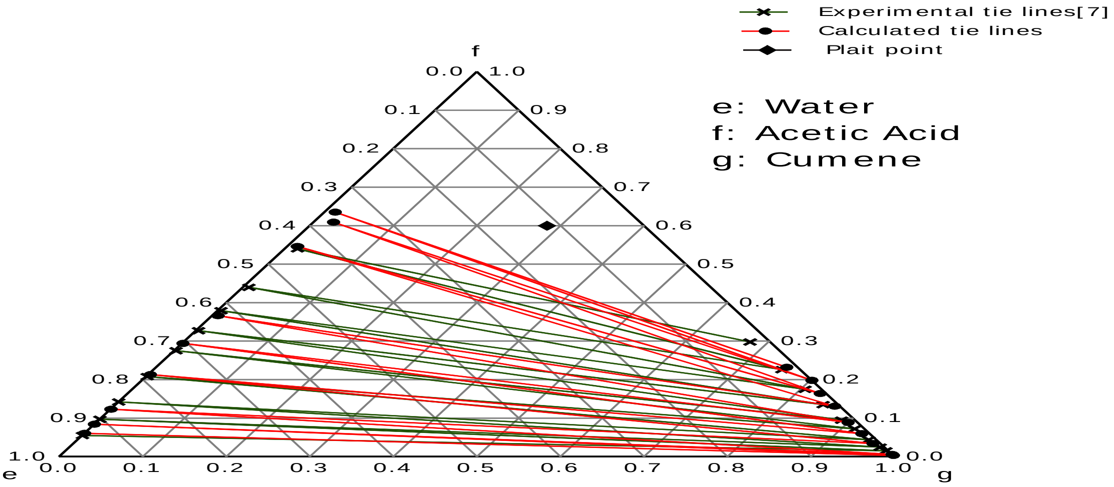

Figure 4.7: Liquid-liquid equilibrium data for system water-acetic acid-cumene at 298.15 K

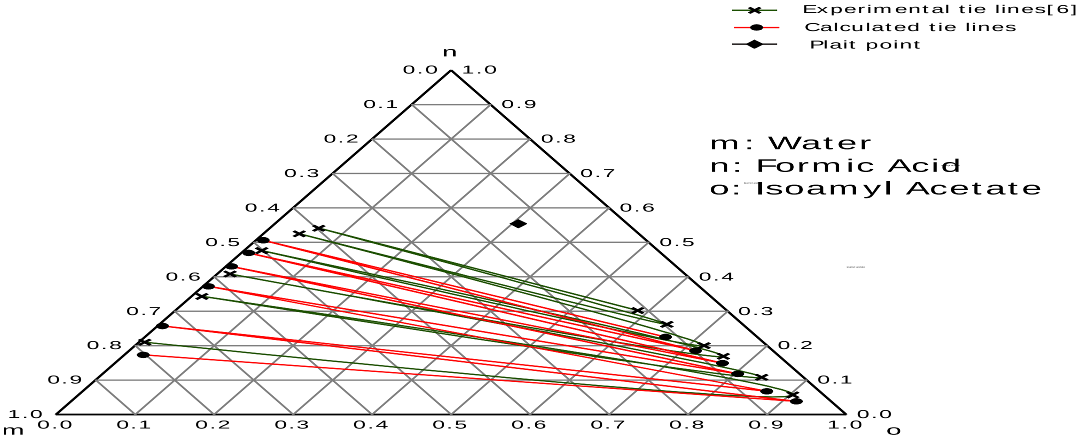

Figure 4.8: Liquid-liquid equilibrium data for system water-formic acid-isoamyl acetate at 298.15 K

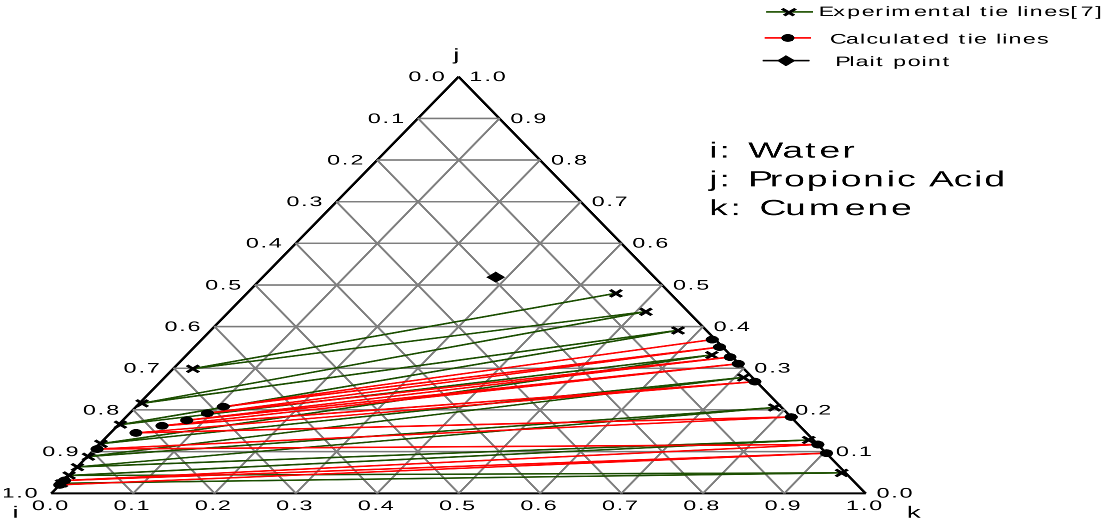

Figure 4.9: Liquid-liquid equilibrium data for system water-propionic acid-cumene at 298.15 K

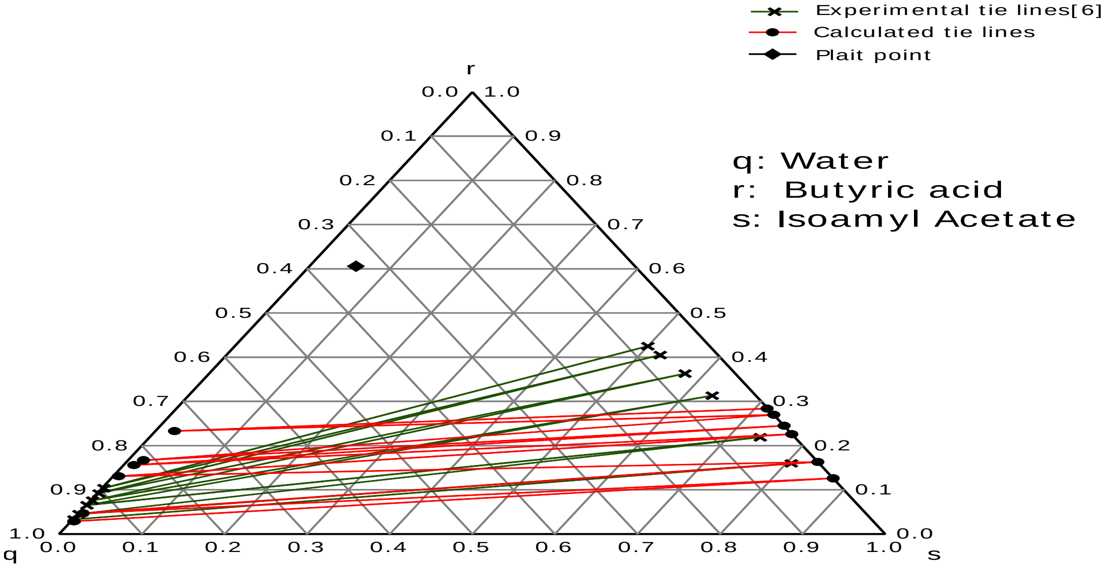

Figure 4.10: Liquid-liquid equilibrium data for system water-butyric acid- isoamyl acetate at 298.15 K

It can be seen that the tie lines predicted by the model in Figure 4.10 tend to be straight segments, it can be explained this, that the mass fractions of butyric acid in the organic phase obtained by the model are somewhat lower than those found for propionic acid.

4.4 Conclusion

In this work we have included the first dissociation of chosen organic acids in the prediction of phase equilibrium. We have divided the studied systems into subsystems to determine the interaction parameters that have been evaluated by the Extended UNIQUAC model. The prediction of the compositions of the components in the two liquid phases is accomplished from binary data available in the literature combined with numerical methods used. Given the inclusion of the dissociation of organic acids in the prediction of the phase compositions compared to authors who did not considered it and given the uncertainty of the experimental data, the prediction results obtained are satisfactory and confirm the applicability of the model for predicting the liquid-liquid equilibrium phase compositions of electrolyte systems using just binary data.

References

[1] Amin, M. I.; Ali, M. M.; Kamal, H. M.; Youssef, A. M.; Akl, M. A. Recovery of high grade phosphoric acid from wet process acid by solvent extraction with aliphatic alcohols. Hydrometallurgy. 105, 115–119 (2010).

[2] Hannachi, A.; Habaili, D.; Chtara, C.; Ratel, A. Purification of wet process phosphoric acid by solvent extraction with TBP and MIBK mixtures. Sep. Purif. Technol. 55, 212–216 (2007).

[3] Gilani, H. G.; Gilani, A. G.; Shekarsaraee, S. Solubility and tie line data of the water-phosphoric acid-solvents at T = 303.2, 313.2, and 323.2 K: An experimental and correlational study. Thermochim. Acta. 558, 36–45 (2013).

[4] Ghanadzadeh, G.; Shekarsaraee, S.; Uslu, H. (Liquid+liquid) equilibrium data of (water+phosphoric acid+solvents) systems at T=(308.2 and 318.2) K. J. Chem. Thermodyn. 53, 52–59 (2012).

[5] Gilani, A. G.; Gilani, H. G.; Ahmadifar, S. Experimental and correlational study of phase equilibria in aqueous mixtures of phosphoric acid with aromatic hydrocarbons at various temperatures. J. Chem. Thermodyn. 91, 121-126 (2015).

[6] Gilani, H. G.; Ghanadzadeh Gilani, A.; Seyed Saadat, S. L. Experimental and correlational study of phase equilibria in aqueous solutions of formic and butyric acids with isoamyl acetate and methyl isoamyl ketone at T = 298.15 K. J. Chem. Eng. Data. 59, 917–925 (2014).

[7] Çehreli, S. Liquid-liquid equilibria of ternary systems (water+carboxylic acid+cumene) at 298.15 K. Fluid Phase Equilib. 248, 24–28 (2006).

[8] Seyed Saadat, S. L.; Ghanadzadeh Gilani, A.; Ghanadzadeh Gilani, H.; Kashef, A.; Fallahi, S. Liquid phase equilibria of aqueous mixtures of carboxylic acids (C1–C4) with ethylbenzene: thermodynamic and mathematical modeling. J. Chem. Eng. Data. 61, 3391–3397 (2016).

[9] Ye, C. Liquid–liquid equilibria for the ternary system containing water+phosphoric acid+organic entrainers at 308.15 and 328.15 K. J. Mol. Liq. 186, 39–43 (2013).

[10] Özmen, D. Determination and correlation of liquid-liquid equilibria for the (water+carboxylic acid+dimethyl maleate) ternary systems at T = 298.2 K. Fluid Phase Equilib. 269, 12–18 (2008).

[11] Gilani, H. G.; Gilani, A. G.; Shekarsaraee, S. Experimental study of phase equilibria in aqueous mixtures of phosphoric acid with isoamyl acetate and methyl isoamyl ketone at T = (298.2, 308.2, and 318.2) K. Fluid Phase Equilib. 337, 32–38 (2013).

[12] Feki, M.; Fourati, M.; Chaabouni, M. M.; Ayedi, H. F. Purification of wet process phosphoric acid by solvent extraction liquid-liquid equilibrium at 25 and 40°C of the system water-phosphoric acid-methylisobutylketone. Can. J. Chem. Eng. 72, 939–944 (1994).

[13] Nicolaisen, H.; Rasmussen, P.; Soerensen, J. M. Correlation and prediction of mineral solubilities in the reciprocal salt system (Na^+, K^+)(Cl^-, SO_4^{2-})-H_2O at 0-100°C. Chem. Eng. Sci. 48, 3149–3158 (1993).

[14] Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems. AIChE J. 21, 116–128 (1975).

[15] Maurer, G.; Prausnitz, J. M. On the derivation and extension of the UNIQUAC equation. Fluid Phase Equilib. 2, 91–99 (1978).

[16] Sander, B. "Extended UNIFAC/UNIQUAC models for (1) gas solubilities and (2) electrolyte solutions," Ph. D. Thesis, Dep. Chem. Eng. Tech. Univ. Denmark, DK-2800 Lyngby Denmark (1984).

[17] Sander, B.; Fredenslund, A.; Rasmussen, P. Calculation of vapour-liquid equilibria in mixed solvent/salt systems using an extended UNIQUAC equation. Chem. Eng. Sci. 41, 1171–1183 (1986).

[18] Guggenheim, EA; Fowler, RH, "Statistical thermodynamics," pp. 422ff, Cambridge Univ. Press. London (1949).

[19] Christensen, S. G.; Thomsen, K. Modeling of vapor -liquid-solid equilibria in acidic aqueous solutions. Ind. Eng. Chem. Res. 42, 4260–4268 (2003).

[20] Yan, W.; Topphoff, M.; Rose, C.; Gmehling, J. Prediction of vapor–liquid equilibria in mixed-solvent electrolyte systems using the group contribution concept. Fluid Phase Equilib. 162, 97–113 (1999).

[21] Anderson, T. F.; Prausnitz, J. M. Application of the UNIQUAC equation to calculation of multicomponent phase equilibria. 1. vapor-liquid equilibria. Ind. Eng. Chem. Process Des. Dev. 17, 552–561 (1978).

[22] Mafra, M. R.; Krähenbühl, M. A. Liquid-liquid equilibrium of (water+acetone) with cumene or α-methylstyrene or phenol at temperatures of (323.15 and 333.15) K. J. Chem. Eng. Data. 51, 753–756 (2006).

[23] Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. Numerical recipes in C++.The art of scientific computing. 2, 1002 (2007).

[24] Moré, J. J. The Levenberg-Marquardt algorithm: implementation and theory. Numerical Analysis. Springer, Berlin, Heidelberg. 630, 105-116. (1978).

[25] Pitzer, K. S.; Silvester, L. F. Thermodynamics of electrolytes: VI. Weak electrolytes including H_3PO_4. J. Solution Chem. 5, 269–278 (1976).

[26] Stig, S.; Stig, W.; Gharib, A. Solvent extraction of phosphoric acid with long

chain tertiary amines. Solvent Extr. Ion Exch. 4, 883–905 (1986).

[27] Bromley, L. A. Thermodynamic properties of strong electrolytes in aqueous solutions. AIChE J. 19, 313–320 (1973).

[28] Elmore, K. L.; Mason, C. M.; Christensen, J. H. Activity of orthophosphoric acid in aqueous solution at 25° from vapor pressure measurements. J. Am. Chem. Soc. 68, 2528–2532 (1946).

[29] Bates, R. G. First dissociation constant of phosphoric acid from 0° to 60° C: limitations of the electromotive force method for moderately strong acids. J. Res. Natl. Bur. Stand. 47, 127–134 (1951).

[30] Pirouzi, A.; Nosrati, M.; Haghtalab, A.; Vasheghani-Farahani, E. Experiment and correlation of osmotic coefficient for aqueous solution of carboxylic acids using NRTL nonrandom factor model. Fluid Phase Equilib. 327, 38–44 (2012).

5. The inclusion of the acetic acid dissociation in the prediction of quaternary liquid-liquid equilibrium (LLE) data

5.1 Introduction

The study of the phase equilibrium of multicomponent electrolyte systems has a practical interest in the separation processes at the industrial level. Since experimental liquid-liquid equilibrium data for mixed-solvent electrolyte systems are not always available, the simulation of industrial chemical processes is required.

Several research works have focused on the application of thermodynamic models to multicomponent electrolyte systems to test their applicability on the phase behavior representation. This applicability was tested by developing the calculation method and studying different types of systems by predicting or correlating the phase equilibrium data.

The thermodynamic modeling is essential for describing the phase equilibrium of multicomponent electrolyte systems through the use of accurate models. The thermodynamic models extended to electrolyte systems (NRTL, UNIQUAC, WILSON) allow describing the influence of the ionic species on the thermodynamic equilibrium of a system.

Despite the considerable research works presented in the literature devoted to the modeling of quaternary systems containing organic components, the physicochemical aspects of these components did not take into account in the phase equilibrium calculations.

For a precise determination of the compositions of phases in equilibrium, it is necessary to consider the dissociation of a solute in the thermodynamic modeling. The purpose of this work is to predict the liquid-liquid equilibrium data for both cases with and without considering the dissociation of the acetic acid and compare the obtained equilibrium data for both cases with the experimental data reported by K. Tamura et al. [1]. The Extended UNIQUAC model was used to predict the LLE data of the quaternary system composed of water-acetic acid-cyclohexane-ethyl acetate system at 298.15 K for both cases. The interaction parameters for the completely miscible binaries are adjusted using the vapor–liquid equilibrium data and the liquid-liquid equilibrium data (mutual solubility) are used to determine the interaction parameters for the partially miscible binaries.

5.2 Thermodynamic modeling

In this work, we use the UNIQUAC model extended version to the electrolyte solutions. The activity coefficient of the Debye-Hückel term for an ionic species (j) and for water is given as follows:

$$\ln\gamma_j^{D-H} = -z_j^2 \frac{A\sqrt{I}}{1+b\sqrt{I}} \tag{5-1}$$

$$\ln\gamma_W^{D-H} = M_W \frac{2A}{b^3}\left[1+b\sqrt{I} - \frac{1}{1+b\sqrt{I}} - 2\ln(1+b\sqrt{I})\right] \tag{5-2}$$

M_W is the molecular weight of water, $b = 1.5\,(\mathrm{Kg\ mol^{-1}})^{1/2}$ is a constant and A is the Debye-Hückel parameter:

$$A = \begin{bmatrix} 1.131 - 1.335*10^{-3}*(T-273.15)+ \\ 1.164*10^{-5}*(T-273.15)^2 \end{bmatrix} \mathrm{kg}^{1/2}\ \mathrm{mol}^{-1/2} \tag{5-3}$$

The ionic strength I is given by:

$$I = \frac{1}{2}\sum_j z_j^2 m_j \tag{5-4}$$

m_j is the molality and z_j is the charge of ion (j).

The symmetrical activity coefficients of combinatorial and residual terms of component (i) are:

$$\ln\gamma_i^{Com} = \ln\left(\frac{\varphi_i}{x_i}\right) - \frac{\varphi_i}{x_i} + 1 - \frac{Z}{2} q_i \left[\ln\left(\frac{\varphi_i}{\theta_i}\right) - \frac{\varphi_i}{\theta_i} + 1\right] \tag{5-5}$$

$$\ln\gamma_i^{Res} = q_i\left[1 - \ln\left(\sum_j \theta_j \psi_{ji}\right) - \sum_j \frac{\theta_j \psi_{ij}}{\sum_l \theta_l \psi_{lj}}\right] \tag{5-6}$$

Z=10 is the co-ordination number, x_i is the mole fraction, φ_i and θ_i are respectively volume and surface area fractions of component (i):

$$\varphi_i = \frac{r_i x_i}{\sum_k r_k x_k} \qquad \theta_i = \frac{q_i x_i}{\sum_k q_k x_k} \tag{5-7}$$

r_i and q_i are respectively volume and surface area parameters of component (i). The interaction parameter ψ_{ji} is given by:

$$\psi_{ji} = \exp\left(-\frac{\Delta u_{ji}}{RT}\right) \tag{5-8}$$

T is the absolute temperature and R is the ideal gas constant. Δu_{ji} is the binary interaction parameters.

The unsymmetrical activity coefficients of combinatorial and residual terms of component (i) are:

$$\ln\gamma_i^{\infty,\mathrm{Com}} = \ln\left(\frac{r_i}{r_w}\right) - \frac{r_i}{r_w} + 1 - \frac{Z}{2} q_i \left[\ln\left(\frac{r_i q_w}{r_w q_i}\right) - \frac{r_i q_w}{r_w q_i} + 1\right] \qquad \textbf{(5-9)}$$

$$\ln\gamma_i^{\infty,\mathrm{Res}} = q_i\left[1 - \ln\left(\psi_{wi}\right) - \psi_{iw}\right] \qquad \textbf{(5-10)}$$

The activity coefficient of a solvent molecule (water) (k) is obtained by the addition of these terms:

$$\ln\gamma_k = \ln\gamma_k^{\mathrm{D-H}} + \ln\gamma_k^{\mathrm{Com}} + \ln\gamma_k^{\mathrm{Res}} \qquad \textbf{(5-11)}$$

The activity coefficient of ionic species (j) is obtained by the addition of these terms:

$$\ln\gamma_j = \ln\gamma_j^{\mathrm{D-H}} + \ln\gamma_j^{\mathrm{Com}} - \ln\gamma_j^{\infty,\mathrm{Com}} + \ln\gamma_j^{\mathrm{Res}} - \ln\gamma_j^{\infty,\mathrm{Res}} \qquad \textbf{(5-12)}$$

5.3 Results and discussion

We are interested in this work to predict the quaternary liquid-liquid equilibrium data from binary parameters. We have used the Extended UNIQUAC model mentioned in the previous section to predict the equilibrium phase compositions with and without considering the dissociation of the acetic acid in the aqueous phase. Different types of data were used to obtain the model parameters for the aim to predict the thermodynamic properties in the first case for H_2O-CH_3COOH-C_6H_{12}-$C_4H_8O_2$, and in the second case for H_2O-CH_3COOH-C_6H_{12}-$C_4H_8O_2$-(H^+, CH_3COO^-). In the second case, the first dissociation of the acetic acid was considered in the thermodynamic modeling to study the influence of this consideration on the phase behavior representation for H_2O-CH_3COOH-C_6H_{12}-$C_4H_8O_2$ and to test the applicability of the model in the prediction of quaternary LLE data including the dissociation of the acetic acid.

The reported data in the literature concerning the vapor–liquid equilibrium data are used to adjust the interaction parameters for the completely miscible binaries as well as the liquid-liquid equilibrium data (mutual solubility) are exploited to determine the interaction parameters for the partially miscible binaries. In the next sections, we will discuss the calculation methods used for each subsystem. The volume and surface area parameters of components reported in [1, 2, 3, 4] are used.

5.3.1 Modeling vapor-liquid equilibrium

The vapor-liquid equilibrium data reported in [5, 6, 7] are used to determine the interaction parameters for ethyl acetate-acetic acid, ethyl acetate-cyclohexane and cyclohexane-acetic acid. The numerical method in [8] was used to obtain the optimal parameters by minimizing the following equation:

$$F(P) = \sum_{i=1}^{N}\left[\left(P^{\mathrm{cal}}(P) - P^{\mathrm{exp}}\right)_i^2\right] \qquad \textbf{(5-13)}$$

The correlated results are illustrated in the Figures 5.1-3. The obtained parameters are displayed in the Table 5.1.

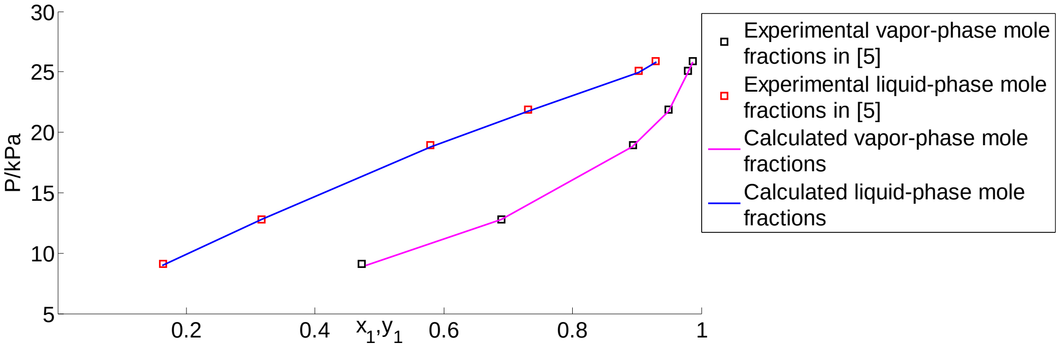

Figure 5.1: Pressure-composition diagram for ethyl acetate(1)-acetic acid(2) binary system at 315.15 K

Figures 5.1-3 show a comparison between the experimental data reported in [5, 6, 7] and the calculated data in this work. Using the Extended UNIQUAC model, isothermal VLE data were calculated for binary systems of ethyl acetate(1)-acetic acid(2) at 315.15 K, ethyl acetate(1)-cyclohexane(2) at 293.15 K and cyclohexane(1)-acetic acid(2) at 298.15 K. Table 5.1 summarizes the absolute relative deviation between the experimental and calculated pressures, as well as the mean absolute deviations between the calculated and experimental compositions for the vapor and liquid phases. The obtained results are coherent with the experimental data.

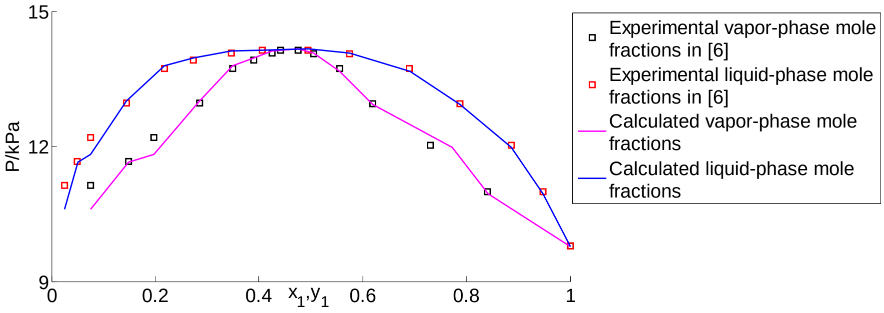

Figure 5.2: Pressure-composition diagram for ethyl acetate(1)-cyclohexane(2) binary system at 293.15 K

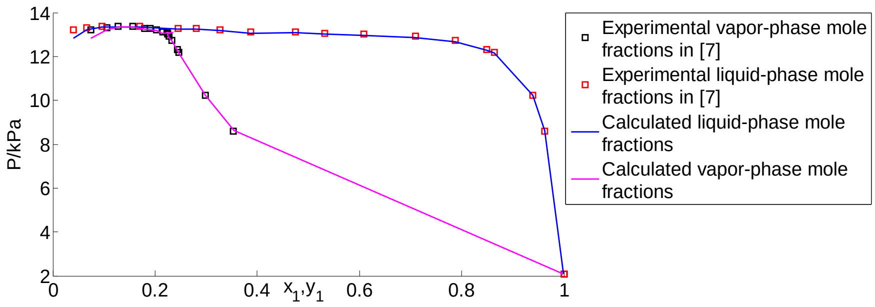

Figure 5.3: Pressure-composition diagram for cyclohexane(1)-acetic acid(2) binary system at 298.15 K

Table 5.1: Correlated results of vapor-liquid equilibrium data

Subsystem (i)-(j)	Temperature (K)	Number of data points	Interaction parameters		Deviations from experimental data reported in [5, 6, 7]		
			Δu_{ij}	Δu_{ji}	$\Delta P^{a,ARD}$	$\Delta y_1^{b,MAD}$	$\Delta x_1^{c,MAD}$
Ethyl acetate(i)-acetic acid(j)	315.15	6	258.39	518.55	0.00629	0.00110	0.00006
Ethyl acetate(i)-cyclohexane(j)	293.15	15	984.03	1968.06	0.00754	0.00313	0.00020
Cyclohexane(i)-acetic acid(j)	298.15	18	448.44	906.77	0.00464	0.00125	0.00004

$$^{a}\Delta P = \frac{\sum_k \left(\frac{\left| P_{exp} - P_{cal} \right|}{P_{exp}} \right)_k}{N} \quad ^{b}\Delta y_i = \frac{\sum_k \left| y_{i,exp} - y_{i,cal} \right|_k}{N} \quad ^{c}\Delta x_i = \frac{\sum_k \left| x_{i,exp} - x_{i,cal} \right|_k}{N}$$

[ARD] Absolute relative deviation

[MAD] Mean absolute deviation

5.3.2 Modeling liquid-liquid equilibrium (Mutual solubilities)

The liquid-liquid mutual solubilities data reported in [9, 10] between water-ethyl acetate and water-cyclohexane are used to determine the interaction parameters for the partially miscible subsystems by resolving the following equation:

$$G = \sum_i (x_i \gamma_i)^{aq} - (x_i \gamma_i)^{org} \qquad \textbf{(5-14)}$$

The resolution of this system was performed by the numerical method in [11]. The obtained parameters are displayed in Table 5.2.

Table 5.2: Interaction parameters for the partially miscible binaries

Subsystem (i-j)	Temperature (K)	Interaction parameters	
		Δu_{ij}	Δu_{ji}
Water(i)-cyclohexane(j)	298.15	0.13	672.19
Water(i)-ethyl acetate(j)	298.15	-4.07	5.23

5.3.3 Prediction of liquid-liquid equilibrium for the quaternary system

The interaction parameters for the water-acetic acid binary system are taken from K. Tamura et al. [1] in the case where no dissociation of the acetic acid is considered and by taking into account the first dissociation of the acetic acid in the prediction of liquid-liquid equilibrium data, the interaction parameters for the subsystem composed of H_2O-CH_3COOH-(H^+, CH_3COO^-) are taken from A. Noumir et al. [12].

The reported parameters for both cases and the adjusted parameters in the previous sections are used to predict the liquid-liquid equilibrium data for H_2O-CH_3COOH-C_6H_{12}-$C_4H_8O_2$ (first case) and are exploited to determine the interaction parameters between C_6H_{12}-(H^+, CH_3COO^-) and $C_4H_8O_2$-(H^+, CH_3COO^-) in the case where the dissociation of the acetic acid is considered (second case). These parameters were found by modeling the thermodynamic equilibrium of H_2O-CH_3COOH-C_6H_{12}-$C_4H_8O_2$-(H^+, CH_3COO^-) system and obtaining the equilibrium compositions, the objective function (5-15) is minimized by the numerical method in [8].

$$\begin{cases} H = \sum\limits_{i=1}^{Ndata} \sum\limits_{j=1}^{N} \left[(x_j\gamma_j)^{aq} - (x_j\gamma_j)^{org} \right]_i^2 \\ \sum\limits_{j=1}^{N} x_j^{aq} = 1 \\ \sum\limits_{j=1}^{N} x_j^{org} = 1 \end{cases} \qquad \textbf{(5-15)}$$

N is the number of components and Ndata is the number of tie lines.

$$RMSD = \sqrt{\frac{\sum\limits_{i=1}^{Ndata} \sum\limits_{j=1}^{N} (x_{ji}^{aq,exp} - x_{ji}^{aq,cal})^2 + (x_{ji}^{org,exp} - x_{ji}^{org,cal})^2}{2 * N * Ndata}} \qquad \textbf{(5-16)}$$

Table 5.3: Interaction parameters and the deviation between the predicted phase compositions for both cases and the experimental data reported in [1]

System	Temperature (K)	Number of tie lines	Interaction parameters				RMSD
Second case			Δu_{35}	Δu_{53}	Δu_{45}	Δu_{54}	
H_2O(1)-CH_3COOH(2)-C_6H_{12}(3)-$C_4H_8O_2$(4)-(H^+, CH_3COO^-)(5)	298.15	21	- 0.048	- 11.96	- 26.32	38.30	0.01040
System First case	Temperature (K)	Number of tie lines	RMSD				
H_2O(1)-CH_3COOH(2)-C_6H_{12}(3)-$C_4H_8O_2$(4)	298.15	21	0.00190				

The standard error between the experimental mass fractions and those calculated for both cases is measured by Root-Mean Square Deviation (RMSD) according to the equation (5-16). Table 5.3 displays the obtained interaction parameters for the second case and the deviations between the experimental mass fractions and those calculated for both cases.

Figure 5.4 illustrates a comparison between the predicted mass fractions for both cases and the experimental mass fractions reported by K. Tamura et al. [1]. In the first case, the predicted liquid-liquid equilibrium data for H_2O-CH_3COOH-C_6H_{12}-$C_4H_8O_2$ are quite satisfactory. The obtained tie lines are approximately comparable to the experimental data reported in [1]. The consideration of the dissociation of the acetic acid in the thermodynamic modeling affects the equilibrium phase compositions especially for water and cyclohexane in the aqueous phase and relatively for the acetic acid in the organic phase. By comparing the predicted mass fractions for water in the aqueous phase for both cases, the predicted mass fractions in the second case differ of those of the first case, which influences the slope of the predicted tie lines. As can be seen in Figure 5.4, the consideration of the dissociation of the acetic acid in the thermodynamic modeling involves an impact on the predicted tie lines for H_2O-CH_3COOH-C_6H_{12}-$C_4H_8O_2$.

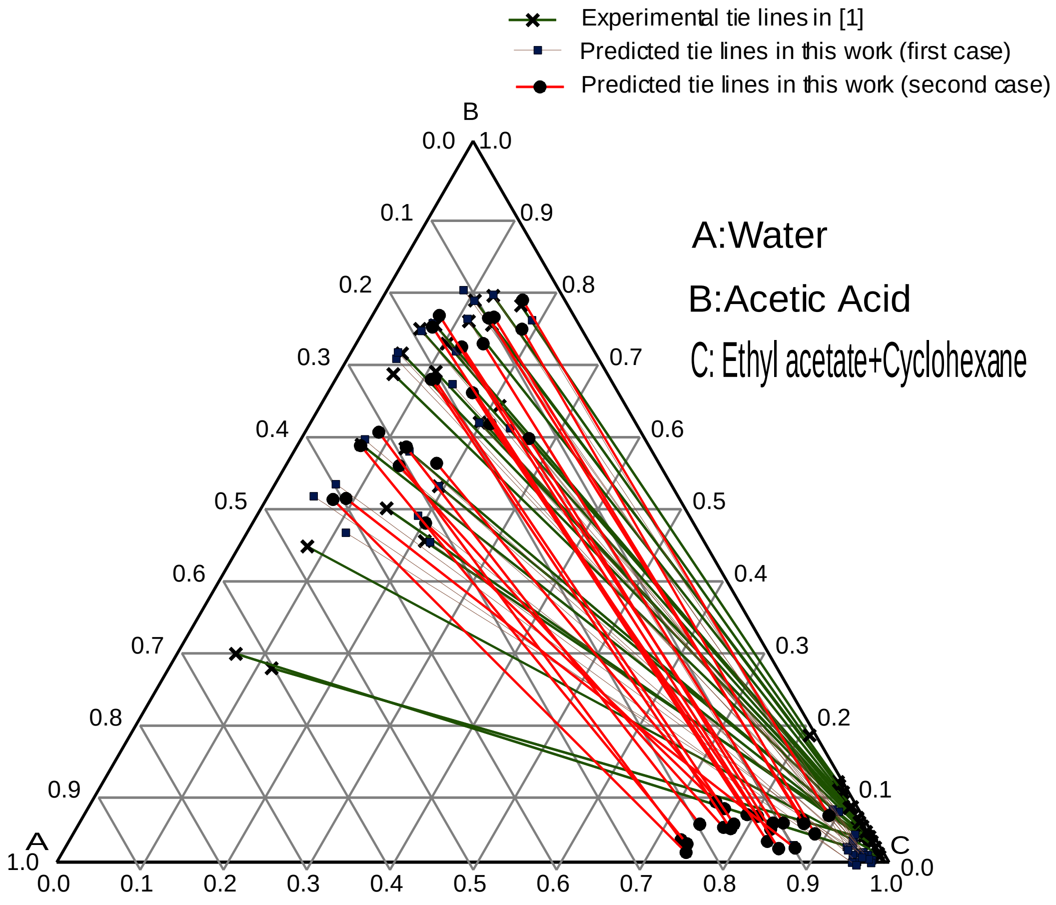

Figure 5.4: Predicted tie lines for both cases for water-acetic acid–cyclohexane-ethyl acetate at 298.15 K

5.4 Conclusion

We have developed in this work the phase equilibrium calculations of the quaternary system composed of water-acetic acid-cyclohexane-ethyl acetate at 298.15 K by including the dissociation of the acetic acid in the aqueous phase in the thermodynamic modeling process. The Extended UNIQUAC model was used to predict the LLE data from binary parameters of the studied quaternary system with and without considering the dissociation of the acetic acid. Despite the change of the slope of the predicted tie lines by including an electrolyte resulting from the dissociation of the chosen organic acid, the obtained LLE data from binary parameters of the studied quaternary system for both cases were satisfactory.

References

[1] Tamura, K.; Morishita, N.; Yamada, T. Ternary and quaternary liquid-liquid equilibria for the water+cyclohexane+ethyl acetate and water+cyclohexane+ethyl acetate+acetic acid systems at the temperature 298.15 K. J. Chem. Eng. Data. 45, 555–558 (2000).

[2] Seyed Saadat, S. L.; Ghanadzadeh Gilani, A.; Ghanadzadeh Gilani, H.; Kashef, A.; Fallahi, S. Liquid phase equilibria of aqueous mixtures of carboxylic acids (C 1 – C 4) with ethylbenzene: thermodynamic and mathematical modeling. J. Chem. Eng. Data. 61, 3391–3397 (2016).

[3] Anderson, T. F.; Prausnitz, J. M. Application of the UNIQUAC equation to calculation of multicomponent phase equilibria. 1. vapor-liquid equilibria. Ind. Eng. Chem. Process Des. Dev. 17, 552–561 (1978).

[4] Yan, W.; Topphoff, M.; Rose, C.; Gmehling, J. Prediction of vapor–liquid equilibria in mixed-solvent electrolyte systems using the group contribution concept. Fluid Phase Equilib. 162, 97-113 (1999).

[5] Dortmund Data Bank for Mixture Data of ethyl acetate+acetic acid at 315.15 K. Retrieved from (DDB Explorer Edition), DDBST GmbH. http:// www.ddbst.com.

[6] Dortmund Data Bank for Mixture Data of ethyl acetate+Cyclohexane at 293.15 K. Retrieved from (DDB Explorer Edition), DDBST GmbH. http:// www.ddbst.com.

[7] Lark, B. S.; Banipal, T. S.; Singh, S.; Palta, R. C. Excess Gibbs energy for binary mixtures containing carboxylic acids. 1. Excess Gibbs energy for acetic acid+cyclohexane,+benzene, and+n-heptane. J. Chem. Eng. Data. 29, 277–280 (1984).

[8] Moré, J. J. The Levenberg-Marquardt algorithm: implementation and theory. Numerical Analysis. Springer, Berlin, Heidelberg. 630, 105-116. (1978).

[9] Richon, D.; Viallard, A. Water/ester systems. II. Solubility studies. Fluid Phase Equilib. 21, 279–293 (1985).

[10] Plačkov, D.; Štern, I. Liquid-liquid equilibria for ternary systems of cyclohexane-water and C1 to C3 alcohols: data and predictions. Fluid Phase Equilib. 71, 189–209 (1992).

[11] Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. Numerical recipes in C++.The art of scientific computing. 2, 1002 (2007).

[12] Noumir, A.; El hami, K.; Saad, B. The inclusion of organic acids dissociation in the prediction of liquid-liquid equilibrium data. Calphad Comput. Coupling Phase Diagrams Thermochem. 62, 92–98 (2018).

6. Modeling of isobaric vapor-liquid equilibrium (VLE) for binary systems

6.1 Introduction

Much attention has been consecrated the area of thermodynamic modeling in the research works of various systems in the last years. These studies were often based on the development of thermodynamic models in order to determine the thermodynamic properties of the systems envisaged.

Because of its important role in chemical engineering in terms in studying, optimizing and controlling in distillation processes, many publications have been focussed on modeling of vapor-liquid equilibrium of varied systems that should be apt encountered in chemical industries.

A precise description of phase equilibrium of mixtures is an essential part of thermodynamic modeling. This requires the utilization of accurate and reliable thermodynamic model. That’s why a great deal of work has been devoted to the development of thermodynamic models for studying and determining the phase equilibrium data of various mixtures.

Despite the large number of studies in the literature pertaining to correlate experimental data of vapor-liquid equilibrium of various systems, but often do not provide enough information in the result of correlation. For example in the modeling of vapor-liquid equilibrium at pressure constant, these works have been not donate the deviations with respect to all variables which are important for testing the accurate of the model used.

In this work, we are interested to apply the Extended UNIQUAC model for modeling the isobaric vapor-liquid equilibrium for methanol-water, methanol-ethanol and ethanol-cyclohexane binary systems at 101.3 kPa, for studying the performance of the model. We signal that we have tried to determine the deviations with respect to all variables.

6.2 The thermodynamic model

We have used the Extended UNIQUAC that composed by combinatorial and residual terms. As we have in our study nonelectrolyte systems, only the short-range interactions are tacked into account.

The activity coefficient of combinatorial term of component (i) is:

$$\ln\gamma_i^{\mathrm{Com}} = \ln\left(\frac{\varphi_i}{x_i}\right) - \frac{\varphi_i}{x_i} + 1 - \frac{Z}{2} q_i \left[\ln\left(\frac{\varphi_i}{\theta_i}\right) - \frac{\varphi_i}{\theta_i} + 1\right] \qquad \textbf{(6-1)}$$

The activity coefficient of residual term of component (i) is

$$\ln\gamma_i^{Res} = q_i\left[1 - \ln\left(\sum_j \theta_j\,\psi_{ji}\right) - \sum_j \frac{\theta_j\psi_{ij}}{\sum_l \theta_l\,\psi_{lj}}\right] \qquad (6\text{-}2)$$

$Z = 10$ is the co-ordination number, x_i is the mole fraction, φ_i and θ_i are respectively volume and surface area fractions of component (i). r_i and q_i are respectively volume and surface area parameters of component (i)

$$\varphi_i = \frac{r_i x_i}{\sum_k r_k x_k} \qquad \theta_i = \frac{q_i x_i}{\sum_k q_k x_k} \qquad (6\text{-}3)$$

The interaction parameter ψ_{ji} is given by:

$$\psi_{ji} = \exp\left(-\frac{\Delta u_{ji}}{RT}\right) \qquad (6\text{-}4)$$

The activity coefficient of component (i) is:

$$\ln\gamma_i = \ln\gamma_i^{Com} + \ln\gamma_i^{Res} \qquad (6\text{-}5)$$

6.3 Results and discussion

As cited previously, we have used the Extended UNIQUAC model. The experimental data reported in the literature for the three binary systems were correlated to adjust the interaction parameters.

Table 6.1: Antoine coefficients

Components	A	B	C	References
Water	7.19	1730.63	-39.72	[1]
Methanol	7.20	1582.27	-33.42	[1]
Ethanol	7.28	1623.22	-44.17	[1]
Cyclohexane	6.85	1206.47	223.13	[3]

Table 6.1 and Table 6.2 summarize the Antoine coefficients and the structural parameters, respectively.

The interaction parameters of methanol-water and methanol-ethanol binary systems were obtained by applying the model to vapor-liquid equilibrium data reported in [1]. The reported data in [2] are used to determine the interaction parameters for ethanol-cyclohexane binary system. The minimization of the Following function (6-6) was carried out by the numerical method in [6] to adjust the interaction parameters for the studied binary systems.

Table 6.2: UNIQUAC structural parameters

Components	r	Q	References
Water	0.92	1.40	[4]
Methanol	1.43	1.43	[4]
Ethanol	2.11	1.97	[4]
Cyclohexane	3.97	3.01	[5]

$$F = \sum_{i=1}^{N}\left[(T^{cal} - T^{exp})_i^2\right] \qquad (6-6)$$

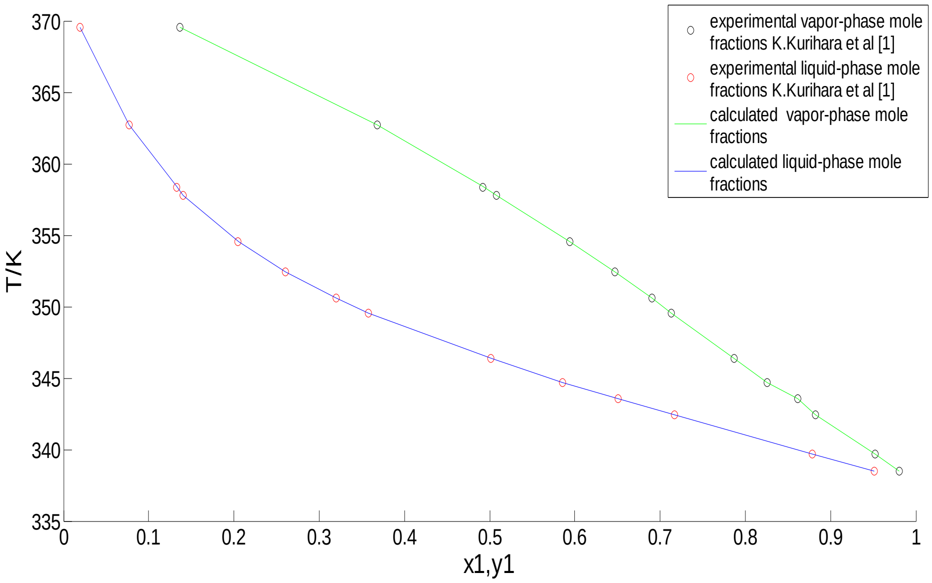

Figure 6.1: Temperature-composition diagram for methanol(1)-water(2) binary system at 101.3 kPa

Table 6.3 presents the obtained interaction parameters. Table 6.4 summarizes the mean absolute deviations between the experimental data and the calculated ones in this work. For a better representation of the experimental data, we have tacked into account to determine the mean absolute deviations with respect to all variables.

Table 6.3: UNIQUAC interaction parameters

Systems	interaction parameters	
	ψ_{ji}	ψ_{ij}
Mehanol-water	9.27	18.54
Methanol-ethanol	10.38	20.76
Ethanol-cyclohexane	13.90	27.81

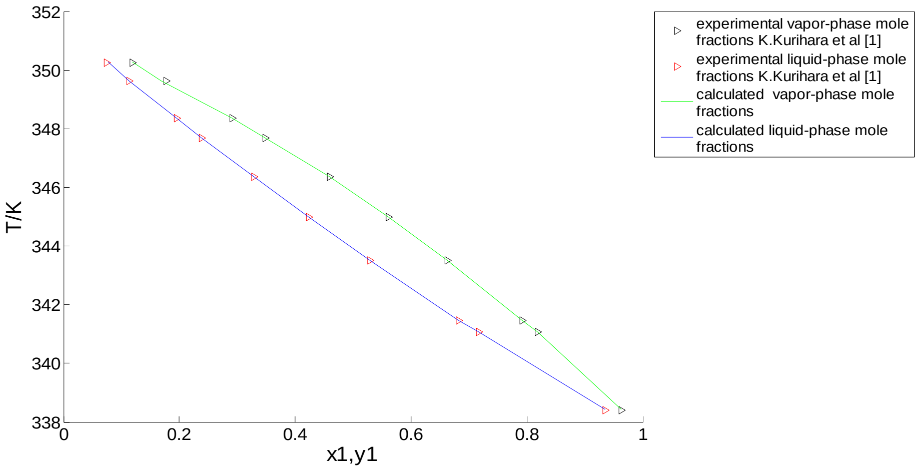

Figure 6.2: Temperature-composition diagram for methanol(1)-ethanol(2) binary system at 101.3 kPa

The calculated and experimental vapor-liquid equilibrium of methanol(1)-water(2), methanol(1)-ethanol(2) and ethanol(1)-cyclohexane(2) data are plotted on (T,x_1,y_1) diagrams in Figures 6.1-3. As can be seen from these Figures, the calculated values are in good agreement with experimental data.

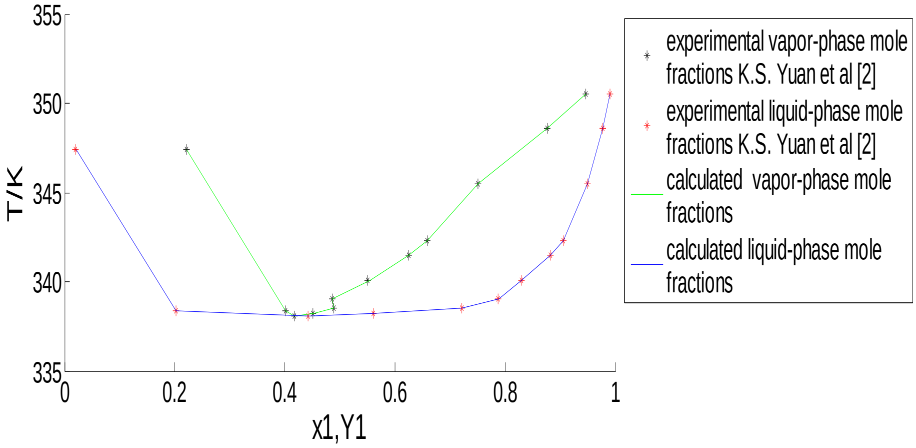

Figure 6.3: Temperature-composition diagram for ethanol(1)-cyclohexane(2) binary system at 101.3 kPa

Table 6.4: Mean absolute deviations between the calculated and experimental data of vapor-phase mole fractions, liquid-phase mole fractions and equilibrium temperatures

System (1)-(2)	Pressure (kPa)	Deviations from experimental data reported in [1, 2]		
		ΔT^a	$\Delta y_1{}^b$	$\Delta x^c{}_1$
Methanol(1)-water(2)	101.3	0.002	0.00007	0.0002
Methanol(1)-ethanol(2)	101.3	0.003	0.0009	0.0004
Ethanol(1)-cyclohexane(2)	101.3	0.0029	0.0007	0.00035

$$\Delta T^a = \frac{\sum_k \left|T_{expt} - T_{calc}\right|_k}{N} \qquad \Delta x_i{}^c = \frac{\sum_k \left|x_{i,expt} - x_{i,calc}\right|_k}{N} \qquad \Delta y_i{}^b = \frac{\sum_k \left|y_{i,expt} - y_{i,calc}\right|_k}{N}$$

6.4 Conclusion

The modeling of isobaric vapor-liquid equilibrium for binary systems is studied in this work. The interaction parameters of the Extended UNIQUAC model for methanol-water, methanol-ethanol and ethanol-cyclohexane were determined by the correlation of the experimental data. A determination of the mean absolute deviations with respect to all variables such as: temperature and compositions in both phases is widely considered for representing the experimental data more better.

References

[1] Kurihara, K.; Nakamichi, M.; Kojima, K. Isobaric vapor-liquid equilibria for methanol+ethanol+water and the three constituent binary systems. J. Chem. Eng. Data. 38, 446-449 (1993).

[2] Shih, Y. K.; Ho, J. C.; Koshpande, AK.; Lu, B. C-Y. Vapor-Liquid Equilibria. J. Chem. Eng. Data. 8, 549-559 (1963).

[3] Cui, Z.; Qian, R.; Yun, Z.; Shi, M. Vapor-liquid equilibria in alcohol+cyclohexane+water systems. J. Chem. Eng. Data. 49, 212-217 (2004).

[4] Anderson, T. F.; Prausnitz, J. M. Application of the UNIQUAC equation to calculation of multicomponent phase equilibria. 1. vapor-liquid equilibria. Ind. Eng. Chem. Process Des. Dev. 17, 552–561 (1978).

[5] Chen, Y.; Wen, C.; Zhou, X.; Zeng, J. Phase equilibria of ternary and quaternary systems containing diethyl carbonate with water. J. Solution Chem. 43, 1374-1387 (2014).

[6] Moré, J. J. The Levenberg-Marquardt algorithm: implementation and theory. Numerical Analysis. Springer, Berlin, Heidelberg. 630, 105-116. (1978).

7. Conclusion

This work was devoted to the thermodynamic modeling of two-phase equilibrium for ternary and quaternary mixtures. To systematically study the separation of organic acids from the aqueous phase to the organic phase via the liquid-liquid equilibrium technique, the effect of chemical equilibrium occurring in the aqueous phase was considered in the modeling of two-phase behavior for multicomponent mixtures. The unexpected presence of ionic species, considering a partial dissociation of organic acids in aqueous solutions, was adopted to simulate the distribution of organic acids between organic phases and aqueous phase solutions.

The separation of organic acids from aqueous solutions was modeled using the Extended UNIQUAC model combined with numerical methods. Initially, binary vapor-liquid and liquid-liquid equilibrium data were used to adjust binary model parameters. For parameters obtained from the correlation of vapor-liquid equilibrium data, the deviations between the experimental and calculated data were determined to test the goodness of the fit. These parameters and the parameters obtained from the mutual solubility data between water and organic solvents were exploited in the modeling of liquid-liquid equilibrium for ternary and quaternary systems.

Phase equilibrium calculations based on solving a set of equations for obtaining phase equilibrium compositions were carried out. The deviations between the calculated data of aqueous- and organic-phase compositions obtained through executing liquid-liquid flash calculations combined with the Extended UNIQUAC model and the experimental data reported in the literature were determined to check the reliability of the model in predicting equilibrium data for multicomponent mixtures including electrolytes. The calculated tie line data were plotted against those of the literature. The applicability of the model was tested in representing nonideal phase behavior of multicomponent mixtures containing organic acids by considering the effect of aqueous species. Despite the deviations of calculated values from experimental values for liquid phase compositions of aqueous and organic two-phase mixtures were relatively high, and although phase diagram representations presented in this work were apparently different for the most of the studied mixtures containing organic acids compared to phase diagram representations of the same mixtures reported in the literature, these differences seem obvious because the effect of the electrostatic interactions was taken into account in this work while this effect was ignored in the works reported in the literature targeted in this thesis.

Appendices

A Calculated results for liquid-liquid equilibrium

A.1 H_2O-H_3PO_4-MIBK at 298.15 K

Aqueous phase			Organic phase		
H_2O	H_3PO_4	MIBK	H_2O	H_3PO_4	MIBK
0.9457	0.0530	0.0013	0.0012	0.0064	0.9924
0.6819	0.3053	0.0128	0.0053	0.0753	0.9194
0.6151	0.3729	0.0120	0.0058	0.0996	0.8945
0.5420	0.4469	0.0111	0.0062	0.1312	0.8626
0.5004	0.4891	0.0105	0.0088	0.1532	0.8381
0.4406	0.5496	0.0098	0.0175	0.1807	0.8018
0.4074	0.5576	0.0351	0.0301	0.2141	0.7558
0.3898	0.5710	0.0392	0.0323	0.2275	0.7402
0.3563	0.6066	0.0370	0.0565	0.2764	0.6671
0.3372	0.6247	0.0381	0.0860	0.3220	0.5920

A.2 H_2O-CH_3COOH-C_9H_{12} at 298.15 K

Aqueous phase			Organic phase		
H_2O	CH_3COOH	C_9H_{12}	H_2O	CH_3COOH	C_9H_{12}
0.9395	0.0605	0.0000	0.0000	0.0032	0.9968
0.9158	0.0842	0.0000	0.0001	0.0059	0.9940
0.8762	0.1233	0.0005	0.0088	0.0342	0.9570
0.7840	0.2135	0.0025	0.0094	0.0597	0.9308
0.7043	0.2939	0.0019	0.0115	0.0888	0.8997
0.6272	0.3658	0.0070	0.0058	0.1308	0.8635
0.4414	0.5464	0.0122	0.0072	0.1643	0.8286
0.3668	0.6093	0.0238	0.0003	0.1978	0.8019
0.3521	0.6350	0.0130	0.0130	0.2321	0.7550

A.3 H_2O-CH_3CH_2COOH-C_9H_{12} at 298.15 K

Aqueous phase			Organic phase		
H_2O	CH_3CH_2COOH	C_9H_{12}	H_2O	CH_3CH_2COOH	C_9H_{12}
0.9799	0.0200	0.0001	0.0000	0.0963	0.9037
0.9689	0.0305	0.0007	0.0000	0.1170	0.8830
0.8904	0.1064	0.0031	0.0002	0.1833	0.8166
0.8238	0.1450	0.0312	0.0014	0.2681	0.7305
0.7836	0.1617	0.0547	0.0018	0.3105	0.6877
0.7459	0.1755	0.0787	0.0027	0.3268	0.6704
0.7124	0.1919	0.0956	0.0035	0.3514	0.6451
0.6851	0.2082	0.1067	0.0041	0.3686	0.6272

A.4 H_2O-HCOOH-$C_7H_{14}O_2$ at 298.15 K

Aqueous phase			Organic phase		
H_2O	HCOOH	$C_7H_{14}O_2$	H_2O	HCOOH	$C_7H_{14}O_2$
0.8035	0.1727	0.0238	0.0440	0.0381	0.9180
0.7370	0.2569	0.0061	0.0666	0.0673	0.8660
0.6208	0.3724	0.0068	0.0782	0.1178	0.8041
0.5628	0.4301	0.0071	0.0820	0.1491	0.7688
0.5215	0.4691	0.0093	0.0984	0.1845	0.7171
0.4843	0.5065	0.0092	0.1159	0.2254	0.6587

A.5 H_2O-$CH_3CH_2CH_2COOH$-$C_7H_{14}O_2$ at 298.15 K

Aqueous phase			Organic phase		
H_2O	$CH_3CH_2CH_2COOH$	$C_7H_{14}O_2$	H_2O	$CH_3CH_2CH_2COOH$	$C_7H_{14}O_2$
0.9679	0.0286	0.0035	0.0001	0.1255	0.8744
0.9476	0.0469	0.0055	0.0001	0.1630	0.8369
0.8629	0.1307	0.0064	0.0002	0.2258	0.7740
0.8310	0.1565	0.0125	0.0003	0.2446	0.7551
0.8149	0.1666	0.0185	0.0005	0.2697	0.7299
0.7438	0.2332	0.0230	0.0006	0.2840	0.7154

A.6 H_2O-$C_4H_8O_2$-CH_3COOH-C_6H_{12} at 298.15 K (first case)

Aqueous phase				Organic phase			
H_2O	$C_4H_8O_2$	CH_3COOH	C_6H_{12}	H_2O	$C_4H_8O_2$	CH_3COOH	C_6H_{12}
0.0269	0.1274	0.0335	0.8122	0.2753	0.1747	0.5317	0.0183
0.0199	0.0913	0.0808	0.8080	0.1827	0.1442	0.6201	0.0530
0.0261	0.0850	0.0839	0.8051	0.1498	0.1349	0.6120	0.1033
0.0351	0.1973	0.0319	0.7357	0.3245	0.1956	0.4543	0.0255
0.0978	0.0345	0.0342	0.8336	0.1248	0.0648	0.7639	0.0465
0.0254	0.0778	0.0230	0.8738	0.2865	0.1180	0.5800	0.0154
0.0206	0.0330	0.0440	0.9024	0.1094	0.0831	0.8037	0.0038
0.0234	0.0379	0.0405	0.8981	0.1612	0.0723	0.7190	0.0474
0.0168	0.0427	0.0488	0.8917	0.1883	0.0824	0.6733	0.0560
0.0139	0.3664	0.0133	0.6063	0.4192	0.0909	0.4676	0.0223
0.0336	0.1255	0.0207	0.8202	0.3204	0.1212	0.4912	0.0673
0.0192	0.0229	0.0246	0.9333	0.0772	0.0448	0.7972	0.0809
0.0155	0.0500	0.0206	0.9138	0.2379	0.0465	0.7087	0.0069
0.0330	0.0434	0.0110	0.9127	0.3318	0.0607	0.5968	0.0108
0.0169	0.0362	0.0095	0.9374	0.2315	0.0398	0.7175	0.0111
0.0200	0.0270	0.0205	0.9325	0.1040	0.0370	0.7891	0.0699
0.0397	0.0920	0.0099	0.8584	0.3973	0.0649	0.5349	0.0029
0.0356	0.0252	0.0274	0.9118	0.0482	0.0499	0.7619	0.1401
0.0361	0.1560	0.0062	0.8016	0.4323	0.0445	0.5182	0.0050
0.0171	0.0313	0.0149	0.9367	0.1888	0.0559	0.7470	0.0083
0.0238	0.0192	0.0173	0.9397	0.1693	0.0312	0.7581	0.0414

A.7 H_2O-$C_4H_8O_2$-CH_3COOH-C_6H_{12} at 298.15 K (second case)

Aqueous phase				Organic phase			
H_2O	$C_4H_8O_2$	CH_3COOH	C_6H_{12}	H_2O	$C_4H_8O_2$	CH_3COOH	C_6H_{12}
0.1556	0.1854	0.0849	0.5741	0.2619	0.1719	0.5638	0.0024
0.1209	0.1263	0.0742	0.6786	0.1703	0.1413	0.6185	0.0698
0.1143	0.1169	0.0564	0.7124	0.1338	0.1301	0.5980	0.1381
0.1611	0.2840	0.0940	0.4608	0.3166	0.2014	0.4808	0.0012
0.0948	0.0345	0.0650	0.8057	0.1232	0.1222	0.7295	0.0251
0.1959	0.1284	0.0633	0.6125	0.2871	0.1183	0.5861	0.0086
0.0689	0.0376	0.0693	0.8242	0.0987	0.1325	0.7651	0.0037
0.1072	0.0488	0.0648	0.7792	0.1512	0.1220	0.7249	0.0018
0.1324	0.0509	0.0765	0.7402	0.1701	0.1325	0.6614	0.0360
0.0979	0.5242	0.0303	0.3476	0.3952	0.0886	0.5148	0.0013
0.1697	0.2323	0.0589	0.5391	0.3087	0.1256	0.5602	0.0054
0.0644	0.0219	0.0499	0.8639	0.0663	0.0947	0.7497	0.0893
0.1550	0.0455	0.0634	0.7360	0.2063	0.1107	0.6798	0.0032
0.2291	0.0717	0.0419	0.6573	0.3098	0.0777	0.6068	0.0057
0.1618	0.0320	0.0572	0.7490	0.2102	0.1021	0.6801	0.0075
0.0704	0.0253	0.0642	0.8402	0.0917	0.1215	0.7664	0.0205
0.2250	0.1549	0.0359	0.5842	0.3410	0.0692	0.5882	0.0016
0.0347	0.0252	0.0752	0.8649	0.0456	0.1427	0.7900	0.0217
0.2321	0.2740	0.0242	0.4698	0.4114	0.0511	0.5136	0.0239
0.1268	0.0276	0.0393	0.8063	0.1725	0.0744	0.7527	0.0004
0.1182	0.0254	0.0305	0.8259	0.1561	0.0561	0.7686	0.0192

B Calculated results for aqueous solutions of organic acids

B.1 Aqueous phosphoric acid solutions at 298.15 K

φ	m_{AC}	m_{A^-}
1.0929	4.00E-02	1.50E-05
0.5539	4.05E-02	1.70E-05
0.5819	6.40E-02	1.71E-05
0.6874	1.01E-01	1.90E-05
0.6744	1.24E-01	1.92E-05
0.6025	1.33E-01	1.96E-05
0.6368	1.64E-01	2.00E-05
0.5724	1.90E-01	2.11E-05
0.6289	2.32E-01	2.20E-05
0.7799	1.51E+00	2.44E-05
0.9443	3.53E+00	2.50E-05
1.0036	3.94E+00	1.00E-01
1.2535	1.27E+01	1.03E-01
1.2329	1.31E+01	1.28E-01
1.2597	1.57E+01	1.31E-01

B.1 Aqueous phosphoric acid solutions at 298.15 K (continued)

φ	m_{AC}	m_{A^-}
1.2694	1.57E+01	6.95E-01
1.2605	1.60E+01	9.93E-01
1.2683	1.62E+01	1.25E+00
1.2514	1.63E+01	1.30E+00
1.2924	1.78E+01	1.45E+00
1.2266	1.78E+01	1.47E+00

B.2 Aqueous acetic acid solutions at 298.15 K

φ	m_{AC}	m_{A^-}
1.0890	6.11E-02	1.33E-12
1.0170	7.88E-02	1.22E-08
1.0007	1.07E-01	1.57E-07
0.9782	1.30E-01	1.92E-06
0.9734	1.73E-01	2.55E-05
0.9576	2.08E-01	3.13E-04
0.9248	2.39E-01	4.00E-03
0.8840	3.12E-01	5.37E-03
0.8553	3.49E-01	6.15E-03
0.7763	4.51E-01	8.50E-03
0.7320	5.40E-01	1.05E-02
0.6609	6.53E-01	1.35E-02
0.5448	8.19E-01	1.92E-02
0.3839	8.63E-01	2.64E-02

B.3 Aqueous butyric acid solutions at 298.15 K

φ	m_{AC}	m_{A^-}
1.0671	5.75E-02	1.02E-05
1.0534	7.61E-02	1.36E-05
1.0138	1.30E-01	2.37E-05
0.9499	1.72E-01	3.30E-05
0.8942	2.53E-01	5.03E-05
0.7557	3.71E-01	8.34E-05
0.6001	5.09E-01	9.14E-05
0.5790	5.81E-01	1.10E-04
0.5164	6.17E-01	1.78E-04
0.4780	7.02E-01	2.11E-04
0.4028	7.32E-01	2.29E-04
0.3522	8.04E-01	2.45E-04
0.3049	8.92E-01	3.74E-04
0.2793	9.44E-01	3.95E-04

B.4 Aqueous formic acid solutions at 298.15 K

φ	m_{AC}	m_{A^-}
0.9956	8.94E-02	6.80E-05
1.0627	1.90E-01	1.33E-05
1.0954	2.31E-01	1.57E-04
1.1160	2.83E-01	1.99E-03
1.1569	3.70E-01	2.47E-03
1.1785	4.36E-01	2.84E-03
1.1998	5.23E-01	3.30E-03
1.2346	7.29E-01	4.37E-03
1.2612	8.80E-01	5.09E-03
1.2824	9.81E-01	5.52E-03
1.3434	1.21E+00	6.36E-03
1.4142	1.69E+00	8.12E-03
1.4508	1.90E+00	8.76E-03
1.4989	2.32E+00	9.34E-03

B.5 Aqueous propionic acid solutions at 298.15 K

φ	m_{AC}	m_{A^-}
1.0611	7.43E-02	1.03E-05
1.0369	1.02E-01	1.45E-05
1.0283	1.32E-01	1.87E-05
1.0176	1.69E-01	2.40E-05
1.0001	2.17E-01	3.10E-05
0.9478	2.53E-01	3.77E-05
0.8959	3.33E-01	5.15E-05
0.8035	4.89E-01	8.06E-05
0.7288	6.24E-01	1.10E-03
0.6613	6.60E-01	1.40E-02
0.5565	8.02E-01	1.92E-02
0.5494	8.11E-01	1.94E-02
0.4821	9.12E-01	2.38E-02
0.4411	9.82E-01	2.68E-02

C Calculated results for isothermal vapor-liquid equilibrium

C.1 $C_6H_{12}(1)$-$C_4H_8O_2(2)$ at 293.15 K

P	x_1	y_1	x_2	y_2
10.5970	0.0250	0.0750	0.9750	0.9250
11.6470	0.0505	0.1481	0.9495	0.8519

C.1 C_6H_{12}(1)-$C_4H_8O_2$(2) at 293.15 K (continued)

P	x_1	y_1	x_2	y_2
11.8281	0.0750	0.1971	0.9250	0.8029
13.0097	0.1440	0.2862	0.8560	0.7138
13.7888	0.2180	0.3504	0.7820	0.6496
13.9575	0.2740	0.3902	0.7260	0.6098
14.1179	0.3475	0.4258	0.6525	0.5742
14.1348	0.4051	0.4419	0.5949	0.5581
14.1603	0.4941	0.4760	0.5059	0.5240
14.0652	0.5751	0.5048	0.4249	0.4952
13.6565	0.6905	0.5560	0.3095	0.4440
12.9235	0.7869	0.6190	0.2131	0.3810
11.9840	0.8871	0.7730	0.1129	0.2270
10.9414	0.9481	0.8419	0.0519	0.1581
9.7718	1.0000	1.0000	0.0000	0.0000

C.2 C_6H_{12}(1)-CH_3COOH(2) at 298.15 K

P	x_1	y_1	x_2	y_2
12.8411	0.0405	0.0745	0.9595	0.9255
13.2129	0.0659	0.1065	0.9341	0.8935
13.3419	0.0961	0.1284	0.9039	0.8716
13.3357	0.1698	0.1563	0.8302	0.8437
13.2597	0.2457	0.1798	0.7543	0.8202
13.2377	0.2803	0.1801	0.7197	0.8199
13.1866	0.3276	0.2026	0.6724	0.7974
13.0640	0.3871	0.2145	0.6129	0.7855
13.0899	0.4745	0.2316	0.5255	0.7684
13.0143	0.5325	0.2247	0.4675	0.7753
12.9660	0.6081	0.2248	0.3919	0.7752
12.8682	0.7090	0.2272	0.2910	0.7728
12.6755	0.7875	0.2346	0.2125	0.7654
12.2681	0.8494	0.2434	0.1506	0.7566
12.1434	0.8644	0.2472	0.1356	0.7528
10.2315	0.9395	0.2986	0.0605	0.7014
8.6108	0.9618	0.3550	0.0382	0.6450
2.0757	1.0000	1.0000	0.0000	0.0000

C.3 $C_4H_8O_2$(1)-CH_3COOH(2) at 315.15 K

P	x_1	y_1	x_2	y_2
8.9722	0.1630	0.4790	0.8370	0.5210
12.7847	0.3168	0.6892	0.6832	0.3108
18.7826	0.5796	0.8934	0.4204	0.1066

C.3 $C_4H_8O_2(1)$-$CH_3COOH(2)$ at 315.15 K (continued)

p	x_1	y_1	x_2	y_2
21.7719	0.7312	0.9488	0.2688	0.0512
24.9562	0.9032	0.9787	0.0968	0.0213
25.8223	0.9295	0.9866	0.0705	0.0134

D Calculated results for isobaric vapor-liquid equilibrium

D.1 $CH_3OH(1)$-$H_2O(2)$ at 101.3 kPa

T	x_1	y_1	x_2	y_2
369.5607	0.0192	0.1370	0.9808	0.8630
362.7211	0.0770	0.3682	0.9230	0.6318
358.3815	0.1333	0.4921	0.8667	0.5079
357.7619	0.1401	0.5080	0.8599	0.4920
354.5104	0.2055	0.5941	0.7945	0.4059
352.4533	0.2602	0.6469	0.7398	0.3531
360.8627	0.3105	0.6830	0.6895	0.3170
350.5816	0.3201	0.6900	0.6799	0.3100
349.5400	0.3581	0.7131	0.6419	0.2869
346.3805	0.5017	0.7869	0.4983	0.2131
344.7091	0.5860	0.8260	0.4140	0.1740
343.5898	0.6512	0.8620	0.3488	0.1380
342.4111	0.7172	0.8820	0.2828	0.1180
339.6628	0.8789	0.9520	0.1211	0.0480
338.4636	0.9510	0.9812	0.0490	0.0188

D.2 $CH_3OH(1)$-$C_2H_5OH(2)$ at 101.3 kPa

T	x_1	y_1	x_2	y_2
350.2656	0.0774	0.1192	0.9226	0.8808
349.6351	0.1131	0.1692	0.8869	0.8308
348.3616	0.1950	0.2920	0.8050	0.7080
347.6821	0.2381	0.3491	0.7619	0.6509
346.3535	0.3291	0.4587	0.6709	0.5413
344.9804	0.4241	0.5613	0.5759	0.4387
343.5047	0.5290	0.6633	0.4710	0.3367
341.4731	0.6817	0.7920	0.3183	0.2080
341.0617	0.7170	0.8180	0.2830	0.1820
338.4163	0.9350	0.9629	0.0650	0.0371

D.3 $C_2H_5OH(1)$-$C_6H_{12}(2)$ at 101.3 kPa

T	x_1	y_1	x_2	y_2
347.4208	0.0205	0.2224	0.9795	0.7776
338.3700	0.2024	0.4022	0.7976	0.5978
338.0876	0.4426	0.4183	0.5574	0.5817
338.2517	0.5604	0.4515	0.4396	0.5485
338.5526	0.7225	0.4890	0.2775	0.5110
339.0605	0.7885	0.4862	0.2115	0.5138
340.0816	0.8298	0.5550	0.1702	0.4450
341.4643	0.8823	0.6253	0.1177	0.3747
342.3123	0.9060	0.6583	0.0940	0.3417
345.4802	0.9490	0.7509	0.0510	0.2491
348.5643	0.9783	0.8771	0.0217	0.1229
350.5094	0.9900	0.9473	0.0100	0.0527