Licianne P. S. Rosa, Natan Cruz, Glória M. N. Costa and Karen V. Pontes*

A comparative study of thermodynamic models to describe the VLE of the ternary electrolytic mixture H₂O-NH₃-CO₂

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Abstract: This study aims to ascertain the influence of the activity coefficient model and equation of state for predicting the vapor–liquid equilibrium (VLE) of the multi-electrolytic system $H_2O-NH_3-CO_2$. The non-idealities of the liquid phase are described by the eUNIQUAC and eNRTL models. The vapor phase is modeled with the Nakamura equation, which is compared with the ideal gas assumption. The models are validated with experimental data from literature on total pressure and ammonia partial pressure. Results show that the models UNIQUAC and NRTL without dissociation can only reproduce the experimental conditions in the absence of CO_2 . When the electrolytic term is considered, the eUNIQUAC model is able to reproduce the experimental data with greater accuracy than the eNRTL. The equation of state which describes the vapor phase plays no major role in the accuracy of the VLE prediction in the operational conditions evaluated here. Indeed, the accuracy relies on the activity coefficient, therefore the ideal gas equation can be considered if the non-idealities of the liquid phase are described by a well-tuned model. These findings could be useful for equipment design, flowsheet simulations and large-scale simultaneous optimization problems.

Keywords: electrolytic solution; eNRTL; eUNIQUAC; ideal gas; Nakamura equation.

1 Introduction

Vapor–liquid equilibrium (VLE) of electrolytic systems are usually found in several segments of the chemical industry, such as reaction and separation stages in the urea synthesis process; absorption process to remove CO_2 and H_2S from gaseous streams; extractive crystallization to precipitate salts using organic solvents. In separation units of the synthesis of urea, for example, the description of phase equilibria of the electrolytic mixture $H_2O-NH_3-CO_2$ plays a key role. According to Ramasamy [1]; a better understanding of the VLE allows for (i) energy integration towards self-sufficient processes, since accurate predictions of process streams enthalpies are required, (ii) a reduction in energy expenditure when designing condenser and absorbers because the equilibrium temperature and composition are more precisely predicted. Experimental data at industrial scale are rarely available because the sampling process is usually complex, either due to the severe temperature and pressure conditions, or due to the dissociation of molecules into ions. Thermodynamic models able to describe the equilibrium conditions of ionic mixtures, therefore, are of paramount importance for the process design and operation.

The industrial production of urea occurs by the reaction between ammonia and carbon dioxide under certain temperature and pressure conditions, according to [2]:

$$2NH_3 + CO_2 \leftrightarrows NH_2CONH_2 + H_2O \tag{R.1}$$

^{*}Corresponding author: Karen V. Pontes, Industrial Engineering Graduate Program/Federal University of Bahia. Rua Aristides Novis, nº 02, Federação, Salvador, 40.210-630, BA, Brazil, E-mail: karenpontes@ufba.br

Licianne P. S. Rosa, Natan Cruz and Glória M. N. Costa, Industrial Engineering Graduate Program/Federal University of Bahia. Rua Aristides Novis, nº 02, Federação, Salvador, 40.210-630, BA, Brazil. https://orcid.org/0000-0002-4662-5933 (L.P.S. Rosa)

In fact, numerous reactions take place simultaneously due to the chemical balance between water, carbon dioxide and ammonia [3], as Figure 1 depicts. The molecular species in the solution dissociate themselves generating ions, which in turn can react to produce urea. In the literature, different reaction schemes have been proposed to describe the species dissociation which occurs in the context of reaction R.1, as Table 1 summarizes. The reaction VI (Figure 1) represents the formation of urea which is neglected by Bernardis et al. [6], Goppert and Maurer [7], Kurz et al. [8], Freitas et al. [13] and Jilvero et al. [15]; because its rate is so low that the time needed to achieve the equilibrium conditions is much longer than the residence time in most equipment in a urea plant. As a result, urea is considered an inert component and the system is represented by the ternary mixture $H_2O-NH_3-CO_2$. Bernardis et al. [6] further neglect the formation of solid NH_4HCO_3 (bicarbonate) and its dissociation (reaction VII, Figure 1) because they observe that the corresponding thermodynamic equilibrium constant is very small and thus the concentration of the carbonate ion is always very small. This study, therefore, considers the reactions I, II, III and IV.

In the 1970s, Edwards et al. [16] proposed a thermodynamically consistent method to describe the VLE of volatile weak electrolytes in dilute aqueous solutions, including ammonia, carbon dioxide, hydrogen sulfide, sulfur dioxide, and hydrogen cyanide. This model considers mass and charge balances, chemical equilibrium and phase equilibrium. To calculate the VLE in aqueous solution, activity coefficients for the solute and the solvent (water) as well as fugacity coefficients are required to describe the liquid and vapor phases, respectively. Although the activity and fugacity models are system dependent, Edwards' method was used by many authors in the literature as the basis for describing the VLE of electrolytic systems [7,8,9, 11, 13, 15]. According to Edwards et al. [17]; the presence of ions in the vapor phase should only be considered at very high temperatures, consequently the choice of the fugacity model for the vapor phase is not so stiff. On the other hand, the presence of charge in the liquid phase, as shown in Figure 1, causes a great deviation from ideality, therefore the activity model should be carefully chosen. The rigorous modeling of electrolytic systems, therefore, is not a trivial task.

The thermodynamic models most frequently used in literature to describe the VLE of the ternary system $H_2O-NH_3-CO_2$ are summarized in Table 1. The non-idealities of the liquid phase were firstly described by the Pitzer model which is able to describe both weak and strong electrolytes based on a complex virial model with numerous parameters. Goppert and Maurer [7] and Kurz et al. [8] validated the Pitzer model against experimental data and observed that it can predict the VLE data reasonably well at low solute concentrations



Figure 1: Ionic dissociation in the ternary system $H_2O-NH_3-CO_2$.

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Author	Reactions considered	Temperature, pressure and con-	Thermodynamic m	lodel
		centration range	Liquid phase	Vapour phase
Bernardis et al. [4]	$NH_3 + H_2 O \rightleftharpoons NH_4^+ + OH^- CO_2 + H_2 O \rightleftharpoons H^+ + HCO_3^- NH_3 + H_2 OH_3 \hookrightarrow NH_2 COO^- + H_2 OH_2 O \rightleftharpoons H^+ + OH^-$	Temperature: 414 < T < 473 K Pressure: 7 kPa < P < 20 MPa Molality: m _{NH3} from 3.85 to 18.3 mol/kg and m _{Co2} up to 14 mol/kg	eUNIQUAC (from [5])	Nakamura
Bernardis et al. [6]	$NH_3 + H_2 O \rightleftharpoons NH_4^+ + OH^- CO_2 + H_2 O \rightleftharpoons H^+ +HCO_3^- NH_3 + HCO_3^- \rightleftharpoons NH_2 COO^- + H_2 OH_2 O \rightleftharpoons H^+ + OH^-$	Temperature: 414< T < 473 K Pressure: 7 kPa < P < 20 MPa Concentration: not defined	eUNIQUAC (from [5])	Nakamura
Goppert and Maurer [7]	$NH_3 + H_2 O \rightleftharpoons NH_4^+ + OH^- CO_2 + H_2 O \rightleftharpoons H^+ + HCO_3^- HCO_3^- \rightleftharpoons H^+ + CO_3^- NH_3 + HCO_3^- \rightleftharpoons NH_2 COO^- + H_2 O$	Temperature: 333.15 < 7 < 443.15 K Pressures: ≤69 atm Molality: <i>m</i> _{NH3} = 16 and <i>m</i> _{G0} = 13 mol/kg	Pitzer	Nakamura
Krichevsky and Karsa- movsky [8]	$NH_3 + H_2 O \rightleftharpoons NH_4^+ + OH^- CO_2 + H_2 O \rightleftharpoons H^+ + HCO_3^- HCO_3^- \rightleftharpoons H^+ + CO_3^- NH_3 + HCO_3^- \rightleftharpoons NH_2 COO^- + H_2 OH_2 O \rightleftharpoons H^+ + OH^-$	Temperature: $313 < T < 353$ K Pressure: ≤ 6.90 atm Molality: $m_{\rm NH_3} = 6$ and 12 and $m_{\rm CO_3} \leq 10$ mol/kg	Pitzer	Nakamura
Darde et al. [9]	$\begin{split} NH_3 &+ H_2 O \rightleftharpoons NH_4^+ + OH^- CO_2 + H_2 O \rightleftharpoons H^+ + HCO_3 - HCO_3^- \rightleftharpoons H^+ \\ &+ CO_3^- NH_3 + HCO_3^- \rightleftharpoons NH_2 COO^- + H_2 OHCO_3^- + NH_4^+ NH_4 HCO_3 - \\ NH_2 COO^- &+ \rightleftharpoons NH_4^+ \rightleftharpoons NH_2 COONH_4 CO_3^- + 2NH_4^+ \\ &+ H_2 O \rightleftharpoons CO_3 (NH_4) \cdot H_2 O \end{split}$	Temperature: 273 < 7 < 333 K Pressure: ≤98.7 atm Molality: m _{NH3} = 80 mol/kg	eUNIQUAC [9] that is an upgraded of the version proposed by Thomsen and Rasmussen [10])	Soave-Redlich- Kwong (SRK) equation
Que and Chen [11]	$\begin{split} NH_3 + H_2 &O \rightleftharpoons NH_4^+ + OH^- CO_2 + 2H_2 &O \rightleftharpoons \\ H_3 &O^+ + HCO_3^- HCO_3^- \rightleftharpoons H_3 O^+ + CO_3^- NH_3 + HCO_3^- \rightleftharpoons \\ NH_2 &COO^- + H_2 &ONH_4 HCO_3 \rightleftharpoons HCO_3^- + NH_4^+ 2H_2 &O \rightleftharpoons H_3 O^+ + OH^- \end{split}$	Temperature: T > 473 K Pressures: ≤6.90 atm Concentration: w _{NH3} = 0.30 and 0 ≤ w _{r0} , ≤ 1	eNRTL	PC-SAFT
Darde et al. [12]	eUNIQUAC: $NH_3 + H^+ = NH_4^+ CO_2 + H_2O = H^+ + HCO_3^- HCO_3^- =$ $H^+ + CO_3^- NH_3 + HCO_3^- = NH_2COO^- + H_2O$ eNRTL: $2H_2O = H_3O^+ + OH^- CO_2 + H_2O = H^+ + HCO_3^- HCO_3^- = H^+ + CO_3$ $-NH_3 + HCO_3^- = NH_2^- COO^- + H_2ONH_3$ $+H_2O = NH_4^+ + OH^- HCO_3^- + NH_4^+ NH_4 HCO_3$	Temperature: 273 < T < 473 K Pressure: 0 < P < 139 atm Molality: m _{NH3} upto 14.3 mol/kg	eNRTL eUNIQUAC (from [9] that is an upgraded of the version proposed by [10]	Soave-Redlich- Kwong (SRK) equation

Author	Reactions considered	Temperature, pressure and con-	Thermodynamic mo	lab
		centration range	Liquid phase	Vapour phase
Freitas et al. [13]	$NH_3 + H_2O = NH_7^+ + OH^-CO_2 + H_2O = H^+ + HCO_3$ - $HCO_3^- = H^+ + CO_3^-NH_3 + HCO_3^- =$ $NH_2COO^- + H_2OH_2O = H^+ + OH^-$	Temperature: 313 < T < 473 K Pressure: ≤69 atm Molality: m _{NH3} = 16 and	eUNIQUAC (from Thomsen et al. [35]; Thomsen [14])	Nakamura
Jilvero et al. [15]	$NH_3 + H_2 O = NH_4^+ + OH^- CO_2 + 2H_2 O = H_3 O^+ + HCO_3$ $- HCO_3 = H_3 O^+ + CO_3 NH_3 + HCO_3 = NH_2 COO^- + H_2 OH_2 O = H^+ + OH^-$	$m_{CO_2} = 1.0 m_{OV} m_{SC}$ Temperature: 283.15 < 7 < 310.15 K Pressures: 1.13 < P < 1.23 atm Concentration: $w_{NH_3} = 0.05$ and 0.10 and 0.15 < $w_{CO_2} \le 0.75$	eNRTL eUNIQUAC (from [9] that is an upgraded of the version proposed by Thomsen and Rasmussen [10])	PC-SAFT Soave-Redlich- Kwong (SRK) equation

Table 1: (continued)

(molalities of ammonia 2.8 mol/kg at 393.15 K and 3.1–3.8 mol/kg at 373.15 K), but large deviations are observed near the minimum total pressure and at very high solute molalities (molalities of ammonia 12.2 mol/kg at 393.15 K and 12.3 mol/kg at 373.15 K). Later, semi-empirical thermodynamic models for electrolytic solutions based on the concept of local composition, eUNIQUAC [5, 18] and eNRTL [19], were proposed to describe the activity coefficient for electrolytic solutions. The eUNIQUAC, unlike the Pitzer model, considers the water dissociation and has a significantly lower number of temperature dependent parameters [20], which have to be obtained experimentally. Bernardis et al. [4] applied eUNIQUAC to describe the liquid phase of the ternary system H₂O–NH₃–CO₂ and, later, Bernardis et al. [4] included urea in the system, considering it an inert component. Darde et al. [9] extended the validation of the eUNIQUAC model, modified by Thomsen and Rasmussen [10]; to wider range of temperature and pressure. The eNRTL relies on much more complicated expressions and requires greater computational effort. Due to species dissociation, the models which describe the liquid phase become too complex, hindering the use of the model for design, operation and large-scale flowsheet optimizations. A knowledge of when the dissociation of species might be neglected is therefore important because it enables model simplification, encouraging its further use on industrial scale. Although different models for describing the non-idealities of the liquid and vapor phases of the ternary system H_2O -NH₃-CO₂ have been used in literature, there is no agreement about which is the best model to describe this system. Jilvero et al. [15] and Darde et al. [12] compared the models eUNIQUAC and eNRTL to describe the liquid phase: Jilvero et al. [15] observed no significant difference in accuracy, whereas Darde et al. [12] concluded that the eUNIQUAC can more satisfactorily describe the experimental data. The comparison between the thermodynamic models under different operating conditions is crucial to evaluate the predictive capabilities of each model and to define which is the best for a particular application.

As the presence of ions in the vapor phase might be neglected [17], the literature usually employs equations of state without ion specifications. The presence of polar species in the vapor mixture of the system $H_2O-NH_3-CO_2$ have been described by several models such as PC-SAFT (Perturbed-Chain Statistical Associating Fluid Theory [21, 22], and SRK (Soave–Redlich–Kwong [23], as can be seen in Table 1. The PC-SAT equation of state is based on statistical thermodynamics and can be applied for polar and non-polar mixtures. The Nakamura equation, although less complex than the PC-SAFT, still considers the presence of polar and non-polar molecules in the vapor phase. The SRK equation of state, proposed by Soave [23]; on the other hand, requires a modification in the temperature-dependent attractive term to be applied to polar substances and their mixtures [24]. Similarly, with regard to the liquid phase, there is also no agreement in the literature about the most suitable model to describe the vapor-phase and its influence on the overall accuracy of the model.

This study aims to ascertain the best pair of activity coefficient and fugacity models for predicting the vapor–liquid equilibrium of the multi-electrolytic system $H_2O-NH_3-CO_2$. The eUNIQUAC and eNRTL models are compared for describing the liquid phase. The model from Pitzer is not used for comparison due to the huge number of parameters which would hinder its practical implementation. In an attempt to investigate the need and the effect of considering the electrolytes in the liquid phase, the extended models eUNIQUAC and eNRTL are compared to the conventional UNIQUAC and NRTL models. The vapor phase is described by the Nakamura equation as well as by the ideal gas equation. The first is chosen to compute the non-idealities of the vapor phase because it can describe polar species with a reasonable level of complexity. The present study, however, suggests that the ideal gas hypothesis might be valid if a more rigorous model, which considers the presence of electrolytes, describes the liquid phase because there is a synergy between the phases. The model predictions are validated with experimental data available in the literature. The findings of the present study might be useful for further studies, such as equipment design, optimization and control of process in the field of CO_2 capture and storage (CCS) and urea synthesis, for example.

2 Thermodynamic model for the VLE of electrolyte systems

The electrolyte method proposed by Edwards et al. [16] considers that chemical and phase equilibria occur simultaneously. The chemical equilibrium in the liquid phase occurs due to the dissociation of the species in

aqueous solution. The phase equilibrium occurs between the remaining molecular species in the liquid phase and the species in the vapor phase. At very high temperatures, Edwards et al. [17] suggest that electrolytes are also present in the vapor phase and therefore should be considered in the phase equilibrium. For the application in this study the temperature range is from 313 to 353 K. At this condition there is simultaneous solubility of ammonia and carbon dioxide in water so the ions in the vapor phase can be neglected.

The first step when modeling electrolyte systems is to determine the dissociation reactions [16]. As previously discussed, reactions I to IV (Figure 1) are considered. Therefore, the ionic species are HCO_3^- , CO_3^{-2} , NH_4^+ , NH_2COO^- , OH^- and H^+ , and the molecular species, H_2O , NH_3 and CO_2 . To describe phase equilibrium in electrolytic system according to the phase rule, the temperature and total feed of molecular solutes (M_{NH3} , M_{CO2}) are usually specified. Firstly, the chemical equilibrium has to be ensured through component mass balance and charge balance so that the molalities of ions and molecular species in the liquid phase are computed (m_{NH_3} , m_{CO_2} , m_{H_2O} , $m_{NH_4^+}$, $m_{HCO_3^-}$, $m_{CO_3^{-2}}$, m_{H^+} , m_{OH^-} , $m_{NH_2COO^-}$). Secondly, the molalities of the molecular species are converted into molar fractions (x_{NH_3} , x_{CO_2} , x_{H_2O}). Finally, the thermodynamic equilibrium is solved by the determination of the molar fraction in the vapor phase (y_{NH_3} , y_{CO_2} , y_{H_2O}) and the total pressure, *P*. The chemical and phase equilibrium for the system $H_2O-NH_3-CO_2$ is detailed below. (i) Chemical equilibrium

The equilibrium constant of the dissociation reactions (I to IV, according to Figure 1) are defined by:

$$K_{i}(T) = \frac{\prod_{i=1}^{NP} (\gamma_{i} m_{i})^{\nu_{i}}}{\prod_{i=1}^{NR} (\gamma_{i} m_{i})^{\nu_{i}}} i = 1, \dots, 4$$
(1)

where K_i is the chemical dissociation constant of reaction *i*, v_i is the stoichiometric coefficient of component *i*, NP, the number of the species formed in reaction, NR, the number of the species in the reagents of reactions, *m* are the molalities of ionic and molecular species and *y* is the activity coefficient of ionic and molecular species calculated by the thermodynamic models. The correlations for K_i for the system H₂O–NH₃–CO₂ are reported by Edwards et al. [17].

(ii) Phase equilibrium

At phase equilibrium, the fugacity of each component in the vapor phase (\hat{f}_i^V) is equal to the fugacity in the liquid phase (\hat{f}_i^L) . For the water, which is considered the solvent, the equilibrium is expressed by:

$$\hat{p}_{\rm H_2O}^{\nu} y_{\rm H_2O} P = a_{\rm H_2O} f_{\rm H_2O}^{\circ L}$$
⁽²⁾

where $\hat{\phi}_{H_2O}^V$ is the fugacity coefficient, y_{H_2O} is the molar fraction of water in the vapor phase, P is pressure, a_{H_2O} is the activity of water, which is given by $a_{H_2O} = x_{H_2O}y_{H_2O}$, where x_{H_2O} is the molar fraction of water in the liquid phase and γ_{H_2O} , its activity coefficient, and $f_{H_2O}^{\circ L}$ is the fugacity of the water in the liquid at the reference, given by:

$$f_{\rm H_2O}^{\circ L} = \phi_{\rm H_2O}^{\rm sat} P_{\rm H_2O}^{\rm sat} \theta_{\rm H_2O}^*$$
(3)

where $\phi_{H_{2O}}^{sat}$ is the fugacity coefficient of water at the system temperature and at the water saturation pressure $(P_{H_{2O}}^{sat})$ calculated by Antoine's equation and $\theta_{H_{2O}}^*$ is the Poynting correction factor for pressure, computed by $\int_{P_s^{sat}}^{P_r} \frac{\overline{v}_{L_s}}{RT} dP$. The fugacity coefficient is computed by an equation of state, such as the Nakamura equation. If ideal gas is assumed, then $\hat{\phi}_{H_{2O}}^V = 1$. The activity coefficient ($\gamma_{H_{2O}}$) is computed, for example, by eUNIQUAC and eNRTL.

The VLE for the solutes NH₃ and CO₂ are given by:

$$\widehat{\phi}_i^V y_i P = m_i \gamma_i^{(m)} H_{i,s}^{Pr,m} \quad i \in \{ NH_3, CO_2 \}$$

$$\tag{4}$$

where m_i is the molality of component *i*, $\gamma_i^{(m)}$ is its activity coefficient on the molal scale and $H_{i,s}^{Pr,m}$ is its Henry constant in the solvent *s* (water) at the reduced pressure, given by:

$$H_{i,s}^{Pr,m} = H_{i,s}^{P_s^{\text{sat}}} \exp\left(\int_{P_s^{\text{sat}}}^{P_r} \overline{\overline{V}_{l,s}^{\infty}} dP\right)$$
(5)

where $\overline{v}_{l,s}^{\infty}$ is the partial molar volume at the infinite dilution of component *i* in the solvent *s* (water), available in [25]; *R* is the universal gas constant, *T* is temperature, *P* is pressure, which is integrated from the saturation pressure P_s^{sat} to the reduced pressure P_r and $H_{i,s}^{\text{psat}}$ is the Henry constant for component *i* in solvent *s* (water) at the solvent saturation pressure, given by:

$$\ln H_{i,s}^{p_{sat}^{\text{sat}}} = a_i + b_{i/T} + c_i \ln T + d_i T + e_i/T^2$$
(6)

where *a_i*, *b_i*, *c_i*, *d_i*, *e_i* are parameters of component *i*, which are reported by Edwards et al. [17].

The resulting mathematical model consists of two subsystems: chemical equilibrium and thermodynamic equilibrium. The first subsystem consists of n = 7 algebraic equations given by the mass and charge balances as well as chemical equilibrium. Given the solute inlet molalities M_{NH3} and M_{CO2} as well as the temperature, the molalities for all components are calculated $(m_{\text{NH3}}, m_{\text{CO2}}, m_{\text{H2O}}, m_{\text{NH4}^+}, m_{\text{HCO3}^-}, m_{\text{CO3}^{-2}}, m_{\text{NH2COO}^-})$. The second subsystem is composed of four equations (Eqs. (2), (4) and $\sum_{i=1}^{3} x_i = 1$) which enables the calculation of the composition in the vapor phase $(y_{\text{NH3}}, y_{\text{H2O}}, y_{\text{CO2}})$ and the total pressure (*P*) for a given inlet temperature and liquid molar fraction.

As shown in Table 1 the eUNIQUAC and the eNRTL models have been used in the literature to describe the non-idealities for the liquid phase in phase equilibrium for the electrolytic system $H_2O-NH_3-CO_2$. To describe the vapor phase, the ideal gas model is compared with the Nakamura equation, which takes into account polar and non-polar compounds. The following sections briefly describe the thermodynamic models used here.

2.1 Extended UNIQUAC – eUNIQUAC

The eUNIQUAC model is an extension of the original UNIQUAC model [26] to further consider electrolytic systems by adding the Debye–Hückel term, which describes the long-range interactions between the species in solution. Sander et al. [5] proposes the eUNIQUAC which was later upgraded by Thomsen [14] according to:

$$\ln \gamma_{i}(T, x) = \ln \gamma_{i}^{C}(x) + \ln \gamma_{i}^{R}(T, x) + \ln \gamma_{i}^{DH}(T, x)$$
(7)

where *i* is the specie, either molecular or ionic, $\ln y_i^C(x)$ is the combinatorial term, $\ln y_i^R(T, x)$, the residual and $\ln y_i^{DH}(T, x)$, the Debye–Hückel contributions. To calculate the combinatorial term, the pure component parameters, volume (*r_i*) and surface (*q_i*), must be known. The residual term further needs binary interaction parameters: u_{ij}^0 and u_{ij}^t , where u_{ij}^0 does not depend on temperature and u_{ij}^t does. The pure component and the binary iteration parameters required by the eUNIQUAC model for the system H₂O–NH₃–CO₂ are taken from [9]; who reported parameters for temperatures up to 423 K. Tables 2, 3 and 4 show the parameters required by the extended UNIQUAC model for the system H₂O–NH₃–CO₂.

The electrostatic term is computed by the Debye–Hückel equation. For the molecular compounds, including the solvent (water), this term is given by:

$$\ln \gamma_i^{DH}(T,x) = \frac{2A_{\gamma}M_i}{b^3} \left[1 + bI^{0.5} - \frac{1}{1 + bI^{0.5}} - 2\ln(1 + bI^{0.5}) \right]$$
(8)

where M_i is the molecular weight of component *i*, $b = 1.5 (kg/mol)^{0.5}$, A_y is the Debye–Hückel parameter given by Sander et al. [5] and *I* is the ionic strength of the solution, which are respectively given by:

$$A_{\gamma} = 1.131 + 1.335 \cdot 10^{-3} T (\ ^{\circ}\text{C}) + 1.164 \cdot 10^{-5} T (\ ^{\circ}\text{C})^2$$
(9)

	r	q
H ₂ 0	0.92	1.4
NH ₃	1.6292	2.9852
CO _{2(aq)}	0.75	2.45
NH ₄ ⁺	4.8154	4.6028
H ⁺	0.1378	$1 imes 10^{-16}$
OH⁻	9.3973	8.8171
CO3 ²⁻	10.828	10.769
HCO ₃ [−]	8.0756	8.6806
NH ₂ COO ⁻	4.3022	4.1348

Table 2: Pure component parameters for the extended UNIQUAC model [9].

Table 3: Binary interaction parameters (\mathbf{u}_{ii}^0) for the extended UNIQUAC model [9].

	H ₂ O	NH3	CO _{2(aq)}	${\sf NH_4}^+$	\mathbf{H}^+	OH⁻	CO3 ²⁻	HCO3_	NH₂COO [−]
H ₂ 0	0								
NH_3	594.72	1090.8							
$CO_{2(aq)}$	8.8383	2500	302.25						
NH4 ⁺	52.7305	785.98	-424.01	0					
H $^+$	10000	10 ⁹	10 ⁹	10 ⁹	0				
OH⁻	600.5	1733.9	2500	1877.9	10 ⁹	1562.9			
CO3 ²⁻	361.39	524.13	2500	226.6	10 ⁹	1588	1458.3		
HCO ₃ [−]	577.05	534.01	526.305	505.55	10 ⁹	2500	800.01	771.04	
$\rm NH_2COO^-$	28.2779	498.15	2500	44.849	10 ⁹	2500	2500	613.25	3343.1

Table 4: Binary interaction parameters (u_{ii}^t) for the extended UNIQUAC model [9].

	H ₂ O	NH3	CO _{2(aq)}	$\rm NH_4$ $^+$	H ⁺	OH⁻	CO3 ²⁻	HCO ₃ ⁻	NH ₂ COO
H ₂ O	0								-
NH_3	7.1827	7.0912							
$CO_{2(aq)}$	0.86293	0	0.3587						
NH4 ⁺	0.50922	6.1271	8.6951	0					
H ⁺	0	0	0	0	0				
OH⁻	8.5455	0.1364	0	0.34921	0	5.6169			
CO3 ²⁻	3.3516	4.9305	0	4.0555	0	2.7496	-1.3448		
HCO ₃ ⁻	-0.38795	5.3111	-3.734	-0.00795	0	0	1.7241	-0.01981	
$\rm NH_2COO^-$	8.0238	6.6532	0	12.047	0	0	0	3.058	-15.92

$$I = \frac{1}{2} \sum m_i z_i^2 \tag{10}$$

where m_i is the molality of the ionic species and z_i is the charge of specie *i*. The Debye–Hückel contribution for the ionic compounds (HCO₃⁻, CO₃⁻², NH₄⁺, NH₂COO⁻) is computed according to:

$$\ln \gamma_i^{DH}(T,x) = -\frac{z_i^2 A_y I^{0.5}}{1 + b I^{0.5}}$$
(11)

The activity coefficients of the ionic compounds are required by the chemical equilibrium described in Eq. (1).

2.2 Electrolyte-NRTL model

The species in electrolytic systems can be classified into molecular, cationic and anionic. The eNRTL (Non-Random, Two Liquids) model was proposed by Chen et al. [27] and is based on the local composition model as well as on the like-ion repulsion and on local electro-neutrality assumptions (Figure 2).

As presented by Chen and Evans [19]; the Gibbs free energy for aqueous electrolyte solution takes into account two contributions: the long-range ion-ion interactions which exist beyond the immediate vicinity of the ionic species; the local interactions which exist in the local vicinity of every specie. Chen and Evans [19] state that the long-range ion-ion interactions are computed by the asymmetric expression from [28] whereas the local interactions are computed by the NRTL equation. The representation of $\ln \gamma_i$ is given by a combination of the long-range (DH) and the short-range (SR) contribution, as given by:

$$\ln \gamma_i^{\text{ex*}} = \ln \gamma_i^{\text{DH}} + \ln \gamma_{i,SR}^{\text{ex*}}$$
(12)

where the superscript ex* means the excess property in the asymmetric convention.

The term $\ln y_i^{\text{DH}}$ is computed by the Pitzer–Debye–Hückel equation and represents the long-range ion-ion interactions, according to:

$$\ln \gamma_i^{\rm DH}(T,x) = -\left(\frac{1000}{M_s}\right)^{\frac{1}{2}} \frac{A_{\gamma}}{3} \left[\frac{2z_i^2}{\rho} \ln\left(1+\rho I_x^{\frac{1}{2}}\right) + z_i^2 I_x^{\frac{\lambda-y_x^2}{2}}\right]$$
(13)

where M_s is the solvent molecular weight, ρ is the specific mass, z_i is the charge of specie *i* and A_y is the Debye–Hückel parameter, computed by Eq. (9). The ionic strength I_x is calculated according to [29]:

$$I_x = \frac{1}{2} \sum x_i z_i^2 \tag{14}$$

where x_i is the molar fraction of the ionic species and z_i is the charge of specie *i*.

The short range term $\ln y_{i,SR}^{\star}$ is computed by NRTL, as described by Song and Chen [30]. Table 5 shows the interacting parameters as provided by Que and Chen [11]. They cover a wide temperature range from 200 to 600 K.

2.3 Nakamura equation

Nakamura et al. [22] proposed an equation of state with perturbation in the rigid sphere term for gaseous mixtures containing polar and non-polar components. The model was developed from the equation of state from [31] and is represented as:

$$P = \frac{RT}{\nu} \left[\frac{1 + \xi + \xi^2 + \xi^3}{(1 - \xi)^3} \right] - \frac{a^*}{\nu(\nu + c^*)}$$
(15)



Figure 2: Interactions considered by the eNRTL model (Balomenos et al. [36]).

Component i	Component j	τ _{1,ij}	τ _{2,ij}	α _{ij}
H ₂ 0	NH ₃	0.5275	-1022.3	0.1
NH3	H ₂ O	3.0173	-726.72	0.1
H ₂ O	NH_4^+ , HCO_3^-	-3.9505	2860.2	0.2
NH4 ⁺ , HCO3 ²⁻	H ₂ O	3.4774	-1850.6	0.2
H_2O	NH_4^{+} , CO_3^{2-}	3.4273	0	0.2
NH4 ⁺ , CO3 ²⁻	H ₂ O	-2.7182	0	0.2
H ₂ 0	NH_4 $^+$, NH_2COO^-	9.7292	0	0.2
$\rm NH_4$ ⁺ , $\rm NH_2COO^-$	H ₂ O	-4.3814	0	0.2
NH3	NH_4 $^+$, NH_2COO^-	7.3696	0	0.1
$\rm NH_4$ $^+$, $\rm NH_2COO^-$	NH ₃	-4.8826	0	0.1

Table 5: τ_{ij} and α_{ij} (Que and Chen [11]).

where *P* is pressure, *v* is molar volume, *T* is temperature, *R* is the ideal gas constant, a^* represents the length of attractive forces, c^* is a parameter independent from temperature, defined solely for the polar compounds, ξ is the reduced density, which is given by:

$$\xi = \frac{b^*}{4\nu} \tag{16}$$

where the parameter b^* refers to the size of the rigid nucleus of the molecule. The value of c^* has to be slightly greater than zero and less than b^* . The parameters a^* and b^* depend on the temperature, according to:

$$a^* = \alpha + \frac{\beta}{T} \tag{17}$$

$$\log b^* = -\gamma - \delta T \tag{18}$$

where α , β , γ and δ are empirical constants.

For mixtures, the parameters a^* , b^* and c^* are replaced by the mixture parameters a_m , b_m and c_m , which are functions of the pure component parameters, according to:

$$a_m = \sum_{i=1}^{NC} \sum_{J=1}^{NC} y_i y_j a_{ij}$$
(19)

$$b_m = \sum_{i=1}^{NC} y_i \cdot b_i \tag{20}$$

$$c_m = \sum_{i=1}^{NC} y_i \cdot c_i \tag{21}$$

where *NC* represents the number of components, y_i is the molar fraction of component *i* and a_{ij} is given by:

$$a_{ij} = \alpha_{ij} + \frac{\beta_{ij}}{T} \tag{22}$$

$$\alpha_{ij} = \alpha_{ij}^0 + \alpha_{ij}^1 \tag{23}$$

$$\beta_{ij} = \beta_{ij}^0 + \beta_{ij}^1 \tag{24}$$

where the parameters α_{ij} and β_{ij} represent intramolecular attraction forces between molecules *i* and *j*.

The fugacity coefficient, $\hat{\phi}_i^{\nu}$, can be determined by the Nakamura equation according to:

$$\ln\hat{\phi}_{i}^{\nu} = \frac{4\xi - 3\xi^{2}}{(1 - \xi)^{2}} + \frac{b_{i}}{b_{m}} \left(\frac{4\xi - 2\xi^{2}}{(1 - \xi)^{3}}\right) + \frac{-2}{RT\nu} \sum_{j=1}^{NC} y_{j}a_{ij} \cdot \sum_{k=1}^{5} \frac{(-1)^{k}}{(k + 1)} \left(\frac{c_{m}}{\nu}\right)^{k} + 1 + \frac{a_{m}c_{i}}{RT\nu^{2}} \cdot \sum_{k=1}^{4} \frac{(-1)^{k}(k + 1)}{(k + 2)} \left(\frac{c_{m}}{\nu}\right)^{k} + 0.5 - \ln Z$$
(25)

where ξ is the reduced density; *a*, *b*, *c* are model parameters; *R* gases universal constant; *v* is molar mixture volume, *Z* is the compressibility factor. The parameters used by the Nakamura equation for the system H₂O–NH₃–CO₂ are available in [22] for a wide temperature range (273–1023 K) and for pressures up to 5000 psia. Tables 6 and 7 show the parameters used by the Nakamura equation for the system NH₃–CO₂–H₂O (Table 8).

2.4 Preliminary evaluation of extended UNIQUAC and NRTL equations for electrolytes

In order to study the quality of eUNIQUAC and eNRTL in the description of ionic behavior of electrolytic solutions, we carried out a preliminary evaluation of the thermodynamic methods using experimental data of average ionic activity coefficient for the salts NaCl, KNO₃, HCl and NaNO₃, reported by Hamer and Wu [32]. The parameters for the eUNIQUAC and the eNRTL equations are available at [14, 19]; respectively. Figures 3 and 4 show the results of the average ionic activity coefficient *versus* the molality for the above-mentioned salts at 25 °C. The predictions of both equations are very close to the experimental data so that the equations are valid. At low and moderate molalities, both equations describe the system accurately with average deviations around 5%. At high molalities, though, the eNRTL slightly deviates from the experimental data, suggesting a superiority prediction capacity of the eUNIQUAC.

2.5 Validation procedure

The thermodynamic models investigated to describe the VLE for the electrolyte system $H_2O-NH_3-CO_2$ are compared with the experimental data from Kurz et al. [8]. The authors reported the total pressure and partial

Table 6: Pure component parameters for the Nakamura equation [22].

	c *	a *	β	γ	δ
H ₂ O	0.01	3.1307	1161.7	1.5589	$5.93 imes 10^{-5}$
NH ₃	0.01	2.6435	561.63	1.3884	4.67×10^{-5}
C0 ₂	0.00	3.1693	253.17	1.2340	$1.47 imes 10^{-4}$

Table 7: Mixture parameters for the Nakamura equation [22].

	α ⁰	α1	β ⁰	β1
H ₂ O	1.06	2.07	8.40	1153.30
NH ₃	1.83	0.81	13.30	548.30
CO ₂	3.17	0.00	253.17	0.00

Table 8: Binary interaction parameters for the Nakamura equation [22].

α ⁰ _{ij}			
	H ₂ O	NH ₃	C0 ₂
H ₂ O	1.06	1.40	4.36
NH ₃	1.40	1.83	3.10
CO ₂	4.36	3.10	3.17



pressure for the system $H_2O-NH_3-CO_2$ up to 6.9 atm for different temperatures and molalities, as summarized in Table 9. Kurz et al. [8] show experimental data of VLE and solid precipitation as well, here just VLE data are used for the model validation.

The models were simulated in Matlab[®] using an Intel (R), Core (TM) i3-3217U, 4.00 GB RAM computer with operational system 64 bits. The algebraic equations are then solved in Matlab using the native function *fsolve*, which is based on the residual minimization method. Although the eNRTL model is available in Aspen, all the simulations were carried out in Matlab because the eUNIQUAC and the Nakamura models are not available in this commercial simulator. The models developed here can be used for modeling equipment which is not available in the Aspen database.

3 Results and discussion

Firstly, the influence of the species dissociation into ions in the VLE of the system $H_2O-NH_3-CO_2$ is investigated. The conventional UNIQUAC and NRTL models, i.e. Eqs. (7) and (13) without the Debye–Hückel term, are

Temperature (K)	Molalities	range
	M _{NH3}	M _{CO2}
313 K	6.33 and 11.83 molal	0 to 5.38 mola
333 K	6.05 and 11.96 molal	0 to 4.44 molal
353 K	6.83 and 12.00 molal	0 to 3.43 mola

Table 9: The inlet experimental conditions reported by Kurz et al. [8].

employed to predict the activity coefficient in the liquid phase, and the fugacity of the vapor phase is predicted by the Nakamura equation and the ideal gas law. To ascertain the most suitable thermodynamic models to describe the VLE of the ternary system, the activity coefficient models which take into account the electrolytic terms, eUNIQUAC and eNRTL, are compared.

3.1 VLE description without species dissociation (UNIQUAC and NRTL)

The activity coefficients are predicted by the UNIQUAC and NRTL models, and the fugacity by the Nakamura equation and ideal gas law. Therefore, four scenarios are investigated: UNIQUAC and Nakamura (U + Nk); UNIQUAC and ideal gas (U + Ig); NRTL and Nakamura (N + Nk); NRTL and ideal gas (N + Ig). Table 10 shows the deviation between the predicted and experimental total pressure (P_T) and ammonia partial pressure (P_{NH_3}) at different temperatures and molalities of ammonia in the absence of CO₂, $m_{CO_2} = 0$. The model predictions are in good agreement with the experimental data provided by Kurz et al. [8]. The UNIQUAC model is more accurate than the NRTL, regardless the models describing the vapor phase. Higher inlet molalities of ammonia results in higher deviations due to the greater ionic concentration in solution as result of the more pronounced dissociation of ammonia. The deviations tend to decrease with increasing temperature because it weakens intermolecular forces so that more molecules leave the liquid phase, decreasing the rate of dissociation reactions and the concentration of ions. As a consequence, it reduces the non-ideality of the mixture. If just a small amount of CO₂ is present, e.g., 0.72 molal of CO₂ at 6.33 molal of NH₃ and 313 K, the deviations are higher than 40%. Then, the results are not shown here for the sake of simplicity. This indicates that the CO₂ strongly increases the non-ideality of the mixture, then the dissociation of the species has to be considered to accurately describe the VLE of the system H₂O–NH₃–CO₂ under the operating conditions presented in Table 9.

3.2 VLE description with species dissociation (eUNIQUAC and eNRTL)

When the species dissociation into ions is considered, the electrolytic term in the activity coefficient model has to be taken into account. As a result, the following pair of models are considered: eUNIQUAC and Nakamura (eU + Nk); eUNIQUAC and ideal gas (eU + Ig); eNRTL and Nakamura (eN + Nk); eNRTL and ideal gas (eV + Ig). The simulations are carried out over a wide range of CO_2 and NH_3 compositions at three temperatures, according to the experimental conditions from Kurz et al. [8] summarized in Table 9. The predicted total pressure at 313 and 333 K is compared with the experimental data in Figure 5 for increasing molalities of CO_2 . The results at 353 K are very similar to the lower temperatures and are not shown here for the sake of simplicity. The eUNIQUAC is able to predict the experimental data reasonably well over a wide range of compositions,

Molal of NH _{3,} <i>M_{NH3}</i>		Ρ ₇ (a	atm)		P _{NH3} (atm)			P _{NH3} (atm)
	U + Nk	U + Ig	N + Nk	N + Ig	U + Nk	U + Ig	N + Nk	N + Ig
Deviation (%) for 313	К							
6.33	3.20	3.00	3.15	2.96	4.29	4.11	4.19	4.12
11.83	4.26	3.90	11.29	10.89	6.10	5.76	14.14	13.75
Deviation (%) for 333	К							
6.06	1.64	1.28	0.97	1.31	2.42	2.12	1.12	1.40
11.96	2.23	1.58	2.94	2.29	3.90	3.29	4.82	4.20
Deviation (%) for 353	К							
6.83	0.39	0.29	0.92	1.11	0.43	0.99	1.03	1.45
12.00	1.89	0.77	3.42	3.96	4.23	3.23	4.13	4.51

Table 10: Relative deviations (%) of total and ammonia partial pressure when the species dissociation is neglected.

U + Nk, Uniquac and Nakamura; U + Ig, Uniquac and ideal gas; N + Nk, NRTL and Nakamura; N + Ig, NRTL and ideal gas.

regardless of the choice of the equation of state, unlike the eNRTL, as confirmed by the relative deviations which can be seen in Table 11. Greater deviations are observed at higher molalites CO₂, a condition which is associated with more pronounced interactions between the pairs molecule–molecule, molecule–ion and ion–ion. The stronger the interaction, the more complex the system, compromising the prediction of the thermo-dynamic model. Despite the non-linearity of the liquid phase, the results indicate that the model describing the vapor phase plays no major role. When the ideal gas law is assumed, the results from eUNIQUAC corroborate the experimental data, indicating that the activity model can capture the non-idealities of the liquid phase. Although the deviations of eNRTL are higher than eUNIQUAC, the fugacity model does not change the model prediction significantly. The ideal gas assumption is therefore valid if the liquid phase is described by eUNIQUAC.

Although the eNRTL does not fit the experimental data from Kurz et al. [8]; as illustrated in Figure 5 and Table 11, Que and Chen [11] and Jilvero et al. [15] successfully apply the eNRTL model to describe the non-idealities of the liquid phase of the same ternary system. These authors simulate the VLE using Aspen Plus, which estimates the parameters of the eNRTL model so that lower deviations are obtained. The parameters of



Figure 5: Total pressure of the system $H_2O-NH_3-CO_2$ predicted by eN + Nk and eN + Ig and by eU + Nk and eU + Ig at 313 K (a) at 6.33 molal NH_3 and (b) at 11.83 molal NH_3 and at 333 K (c) at 6.05 molal NH_3 and (d) at 11.95 molal NH_3 .

Table 11: Average relative deviation (%) of total pressure when species dissociation is considered.

Molal of NH ₂	eU + Nk	ell + lg	eN + Nk	eN + Ig
Average deviation (%)	T = 212 V			
Average deviation (70)	7 – 515 K			
6.33	6.62	6.42	21.05	20.78
11.83	4.39	5.46	22.79	20.87
Average deviation (%)	<i>T</i> = 333 К			
6.06	2.91	5.38	12.20	12.53
11.96	5.16	7.29	11.22	11.57
Average deviation (%)	T = 353 K			
6.83	5.66	6.05	9.29	9.13
12.00	7.72	8.02	8.35	7.17

the eNRTL used for the simulations presented here, however, are taken from the literature [11] since the parameter estimation is beyond the scope of this paper. Despite this feature of the commercial simulator, its database does not offer either eUNIQUAC nor the Nakamura equation of state, which is why another simulation platform was used here. More accurate predictions could be obtained if the parameters of the eNRTL were estimated from experimental data, as carried out by Prudente et al. [33].

Figure 5 indicates that increasing the CO_2 concentration causes a drop in the total pressure of the system. A higher CO_2 content favors chemical dissociation reactions in the liquid phase, decreasing the concentration of molecular species which vaporize, reducing the vapor pressure. These findings are in accordance with the literature [7, 34]. These authors report pressure decreases until the ammonia in the liquid phase is totally consumed by the dissociation reactions. From that point on, the additional CO_2 stays in the molecular form and can vaporize, thus contributing to the increase in the total pressure. In these conditions, carbon dioxide has to be physically dissolved in an aqueous, nearly non-reactive solution. The results of ammonia partial pressure are very similar to those in Figure 5, so for the sake of simplicity they are not shown here.

4 Conclusion

This study investigates the ability of different thermodynamic models to predict the VLE for the multielectrolytic system $H_2O-NH_3-CO_2$. In the absence of CO_2 , the dissociation into ions can be neglected without loss of accuracy because the conventional UNIQUAC and NRTL models are able to describe the VLE for the mixture ammonia and water. When CO_2 is added to the system, however, the ionic dissociation hast to be considered, therefore the extension models for electrolytes, eUNIQUAC and the eNRTL have to be employed to satisfactorily predict the activity coefficient of the liquid phase. The results show that the fugacity model, which represents the vapor phase, plays no major role at low pressures (<7 bar) because, for a given activity coefficient model, both Nakamura and the ideal gas law results in similar predictions. Therefore, there is no need to use complex equations of state, such as PC-SAFT, to describe the vapor phase, as has been suggested in the literature. The activity coefficient model is indeed important and can capture the non-idealities of the liquid phase. The eUNIQUAC model is simpler and more precise than the eNRTL, even when its parameters are not previously adjusted to the experimental data. Therefore, the pair eUNIQUAC with Nakamura or with the ideal gas to predict the VLE of the electrolytic system $H_2O-NH_3-CO_2$ is recommended. These findings might be useful for the formulation of less complex models for the design and operation of processes which involve ionic species.

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