An approach for VLE model development, validation, and implementation in Aspen Plus for amine blends in CO_2 capture: the HS3 solvent case study

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Abstract

Carbon Capture and Storage (CCS) using chemical absorption is a viable method to significantly cut CO_2 emissions in the industrial and energy sectors. However, further development of improved absorbents is necessary to reduce the costs and environmental impact of current CCS technologies. To design the process and quantify energy consumption and costs through process simulation, it is necessary to implement an accurate and robust thermodynamic model. This article describes in details how to develop, regress, and validate a VLE model using ELECNRTL model in Aspen Plus V11 for the novel HS3 solvent, a blend of 3-amino-1-propanol and 1-(2-hydroxyethyl) pyrrolidine, which is currently being characterized in Realise (H2020-funded project). The VLE model is validated over a wide range of temperatures and loadings. The proposed procedure to regress ELECNRTL parameters can be used as a general guideline for implementing VLE models in Aspen Plus for generic amine blends or electrolyte solutions.

Highlights

- Aspen Plus VLE model implementation approach for AP-PRLD blend for CO_2 capture
- The methodology is general and applicable for developing ELECNRTL models
- Experimental validation using quality in-house VLE data
- Accurate estimation of absorption heat and reasonable speciation plots are obtained
- Estimation of physical properties of the blend

Keywords: amine blends, CO_2 capture, ELECNRTL Aspen Plus, equilibrium model, model validation, chemical absorption.

1. INTRODUCTION

Carbon capture and storage (CCS) is considered a key technology in reducing global carbon dioxide emissions. Considering that industrial sources account for about 16% of the worldwide CO_2 emissions (epa.gov, 2022), installing CO_2 removal facilities to treat the flue gas from those production plants, such as refineries and cement plants, can play a key role in mitigating climate changes. However, the current implementation of CCS technologies at the industrial level is limited, mainly due to high costs (Yamada, 2021). The significant thermal duties required to regenerate conventional amine solvents, such as mono-ethanolamine (MEA) and methyl-diethanolamine (MDEA) may therefore be a limitation for global implementation and deployment. It is, therefore, essential to further improve the efficiency of the overall process by developing innovative solvents with improved capture capacity and lower environmental impact compared to traditional amines

used for CO_2 absorption (Pellegrini et al., 2021). A new aqueous amine blend (the HS3 solvent) which is made up of a primary polyamine (3-amino-1-propanol, named AP) at 15 wt%, and a tertiary amine (1-(2-hydroxyethyl) pyrrolidine, named PRLD) at 40 wt% concentration, has been characterized as part of the Realise project funded by the European Community (Realise, 2022). The experimental tests carried out so far have shown that the CO_2 cyclic capacity of HS3 can be significantly higher than that of 30 wt% MEA. Preliminary analysis indicates that the solvent has a significantly lower regeneration duty compared to the benchmark MEA solvent. An elaborate pilot campaign is also currently being carried out at the Tiller plant (September 2022 - January 2023 in Trondheim, Norway).

The development and validation of first-principle models are essential to accurately model and simulate advanced chemical processes. Such simulation models are used as an important tool for energy-, cost- and design calculations in several fields of chemical- and energy engineering (Bisotti et al., 2022, 2021; Kucka et al., 2003; Liu et al., 2016; Svendsen et al., 2011).

This article presents a procedure to develop and validate an eNRTL (ELECNRTL) VLE model of the Realise HS3 solvent, implemented in Aspen Plus V11 (Aspen Plus®, 2019; Liu et al., 2016). Ancillary models that describe physical properties such as density, viscosity, and heat capacity are provided, as well as the definition of the chemical reaction scheme during CO_2 absorption together with the temperature-dependent equilibrium constants. The developed model has been validated in the temperature range from 40 to 120°C, and for solvent CO_2 loadings from 0.01 up to 1 mol/mol. Uncertainty analysis has been conducted, investigating the model's accuracy against the measured VLE data.

The proposed approach provides a general methodology of implementation, which has not been published earlier. The proposed general approach can, be applied to any ELECNRTL activity coefficients model. The authors would like to remark that the VLE correct representation and prediction is at the base of any capture system, and it affects the design of the two main units (i.e., absorber and regenerator), as well as all other units that require the calculation of the phase equilibrium (i.e., flashes). Details concerning physical property models available in Aspen Plus V11 and the way they are referred to and named in the process simulator are highlighted so that the article can be considered as a detailed implementation guideline to construct an ELECNRTL model in Aspen Plus for reactive liquid-gas systems, such as amine blends used to capture CO_2. The supplemental solvent physical properties and the corresponding models describing these properties are reported in the Supplementary Material.

2. METHODS

An ELECNRTL model is exploited to describe the interactions in the liquid phase in HS3 solvent, while the gas phase is simply modelled as an ideal gas (Antoine equation), in accordance with the theoretical background paragraph (Aspen Plus®, 2019). This approach has already been implemented with successful results for many standard amine-based solvents and it is still the most widely used commercial suite for simulating processes based on mono-ethanolamine (MEA) and methyl-diethanolamine (MDEA). The main steps required to build an ELECNRTL model for a new blend are represented in the flowchart of Figure 1. More specifically, molecule-molecule interactions are firstly described disregarding the formation of ions; in a further step, molecule-ions intercations are described based on the implemented elementary reaction scheme by fitting dedicated ELECNRTL coefficients to VLE data for complete system (amine-H_2O-CO_2). Finally, the obtained VLE model must be tested to check its reliability, accuracy and stability. This diagram also clarifies which are the experimental data exploited in each progressive step.
Table 1 gathers and lists all the parameters that should be implemented to properly define the VLE for amine(s) blends. Moreover, the same table reports the references used to get experimental data and/or

models for some of the parameters implemented in Aspen Plus. For physical properties, please refer to the Supplementary Material.

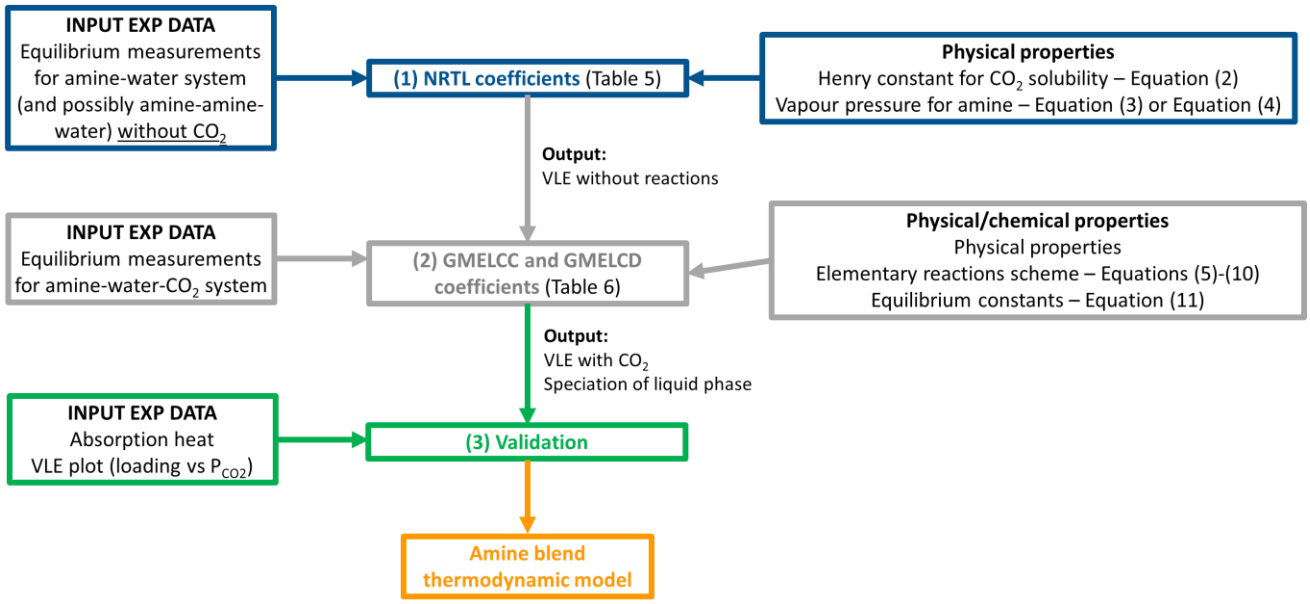


Figure 1. Flowchart summarizing the procedure followed in this work for ELECNRTL model development and validation.

Table 1. List of parameters and thermodynamic properties necessary to properly define ELECNRTL model in Aspen Plus

Property	Model name in Aspen	Parameters regressed in Aspen Plus (corresponding element in the equation)	Model expression	Data sources for fitting
Activity coefficient model (VLE model)	NRTL (molecule-molecule pairs)	NRTL/1 (A_{ij}) NRTL/1 (A_{ji}) NRTL/2 (B_{ij}) NRTL/2 (B_{ji}) NRTL/3 (α_{ij})	$\ln(\gamma_i) = \frac{\sum_{j=1}^{n} x_j \cdot \tau_{ji} \cdot G_{ji}}{\sum_{k=1}^{n} x_k \cdot G_{ki}} + \sum_{j=1}^{n} \frac{x_j \cdot G_{ij}}{\sum_{k=1}^{n} x_k \cdot G_{kj}} \cdot \left(\tau_{ij} - \frac{\sum_{m=1}^{n} x_m \cdot \tau_{mj} \cdot G_{mj}}{\sum_{k=1}^{n} x_k \cdot G_{kj}} \right)$ $G_{ji} = \exp(-\alpha_{ij} \cdot \tau_{ij})$ $\alpha_{ij} = \alpha_{ji} =$ non randomness factor $\alpha_{ij} = 0.1$ (recommended default value in ELECNRTL) $\tau_{ij} = A_{ij} + \frac{B_{ij}}{T}$	Binary AP-H_2O VLE data by: • (Bernhardsen et al., 2019)
	GMELC (molecule-ion and ion-molecule pairs)	GMELCC (A_{ij}) GMELCC (A_{ji}) GMELCD (B_{ij}) GMELCD (B_{ji})		AP-PRLD-CO_2-H_2O data (REALISE, 2022

Vapor pressure	Extended Antoine	PLXANT (C_1, C_2, C_3)	$\ln(P_{sat}[\text{bar}]) = C_1 + \frac{C_2}{T[\text{K}] + C_3}$	AP: • (Green and Perry, 2007) PRLD: • (Bernhardsen et al., 2019)
Henry's constant	Henry's constant	HENRY (A_{ij}, B_{ij}, C_{ij}, D_{ij})	$\ln(He\ [\text{kPa}]) = A_{ij} + \frac{B_{ij}}{T} + C_{ij} \cdot \ln(T) + D_{ij} \cdot T$	(REALISE, 2022)
Reaction equilibrium constant		A B C D	$\ln(K_i) = A + \frac{B}{T} + C \cdot \ln(T) + D \cdot T$	AP: • (Dong et al., 2010) PRLD: • (Li et al., 2017)

2.1 Henry constant

In order to estimate the physical solubility of the pure i-th components, i.e, the CO_2, a Henry correlation (H_i) is used. Therefore, the solubility is part of the requirement of fulfilling the vapor-liquid equilibria relationship between the liquid species and fugacities (f_i^V), see section 2.4.1. For the CO_2, it is important to define this parameter since the affinity between CO_2 and the pure amines and their blends depends on the amines features, which affects both the physical (VLE) and the chemical equilibrium (amines speciation and amount of dissolved CO_2 into the liquid).

Since CO_2 reacts as it contacts an amine, N_2O analogy is the only possible way to estimate the solubility constants as in (1). This approach is widely adopted in the literature (Aronu et al., 2011; Bishnoi and Rochelle, 2000; Sada et al., 1977).

$$H_{CO_2-\text{amine}} = \frac{H_{N_2O-\text{amine}} \cdot H_{CO_2-H_2O}}{H_{N_2O-H_2O}} \quad (1)$$

N_2O solubility data in water, AP and PRLD have been collected within the Realise project in a temperature range between 15°C and 80°C with a step of 5°C. Then, expression (1) was adopted to estimate the Henry constant for CO_2-AP and CO_2-PRLD at every temperature. Finally, Henry's constant temperature dependence is defined according to correlation (2) used in Aspen Plus.

$$\ln(He\ [\text{kPa}]) = A + \frac{B}{T} + C \cdot \ln(T) + D \cdot T \quad (2)$$

The values of parameters A, B, C, and D resulting from the minimization of the relative square deviations between the solubility were calculated based on the experimental solubility data and the model predictions.

2.2 Vapor pressure

The vapor pressure describes the phase equilibrium between the aqueous solution, namely water and the amine(s), and the corresponding vapor phase allowing the prediction of the amine concentration of amines in the vapor phase. Correct description of varpo pressure is also important in design of the water washing section abating the amine traces in the treated gas. The vapor pressure of pure AP and PRLD can be modelled in Aspen Plus exploiting the extended Antoine equation, reported in (3).

$$\ln\left(P_{sat}[\text{bar}]\right) = C_1 + \frac{C_2}{T\,[\text{K}] + C_3} + C_4 \cdot \ln(T\,[\text{K}]) + C_5 \cdot T \tag{3}$$

For simplicity, a standard Antoine equation expression (4) can be be adopted without losing accuracy. For the sake of knowledge, the SRK equation has also been tested. The observed relative differences between the partial pressure of CO2 at given loading and operating temperature obtained with SRK and ideal gas model remained always below 1%.

$$\ln\left(P_{sat}[\text{bar}]\right) = C_1 + \frac{C_2}{T\,[\text{K}] + C_3} \tag{4}$$

The coefficients in Antoine expression can be available in the literature or refitted from experimental data. For what specifically concerns HS3, Antoine coefficients are already available in the literature for AP (Green and Perry, 2007), while the coefficients for PRLD have been fitted to the vapor pressure data collected in Berhardsen (Bernhardsen et al., 2019).

2.3 Elementary reaction schemes and equilibrium constants

Amines react with the absorbed CO_2 following well-established elementary chemical reactions. Primary amine (such as AP) can speciate into the protonate form according to reaction r_4 or turn into their carbamate form as in r_5. In the latter reaction, the CO_2 is fixed into the bicarbonate ion whose formation is described in reaction r_2. Tertiary amine (such as PRLD) can only protonate or deprotonate as in r_6. The scheme of elementary reactions is complete with the self-ionization of water (r_1) and the carbonate formation (r_3). This elementary scheme has already been implemented to characterize several amine blends in Aspen Plus (Dutcher et al., 2015; Kucka et al., 2003; Liu et al., 2016; Yamada, 2021).

Dissociation of water (r_1)	$2H_2O \rightleftharpoons H_3O^+ + OH^-$	(5)
Hydrolysis of carbon dioxide (r_2)	$2H_2O + CO_2 \rightleftharpoons H_3O^+ + HCO_3^-$	(6)
Dissociation of bicarbonate ion (r_3)	$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$	(7)
Protonation of AP (r_4)	$APH^+ + H_2O \rightleftharpoons AP + H_3O^+$	(8)
Carbamate formation (r_5)	$APCOO^- + H_2O \rightleftharpoons AP + HCO_3^-$	(9)
Protonation of PRLD (r_6)	$PRLDH^+ + H_2O \rightleftharpoons PRLD + H_3O^+$	(10)

The equilibrium constant can be expressed as a function of the temperature as in equation (11):

$$\ln(K_i) = A + \frac{B}{T} + C \cdot \ln(T) + D \cdot T \tag{11}$$

For reactions r_1 to r_3, which are not dependent on the specific solvent under investigation, the temperature dependence of the equilibrium constant has been expressed considering literature coefficients (Posey and Rochelle, 1997). For reaction r_4 the coefficients A to D have been regressed starting from the expression

provided in a contribution by Dong et al., 2010, where the equilibrium constant is defined as a function of both temperature and CO_2 loading. Reaction r_5 is the difference between the global reaction for AP r_{glob1} in (12) and reaction r_2 in (6).

Global AP forward reaction (r_{glob1}) $$3\mathrm{A1P} + \mathrm{CO_2} + \mathrm{H_2O} \rightarrow 3\mathrm{A1PCOO^-} + \mathrm{H_3O^+} \quad (12)$$

Due to the properties of logarithms, the equilibrium constant of reaction r_5 is simply given by (13):

$$\ln\left(\mathrm{Keq_{r5}}\right) = \ln\left(\mathrm{Keq_{glob1}}\right) - \ln\left(\mathrm{Keq_{r2}}\right) \quad (13)$$

The temperature dependence of the r_{glob1} reaction equilibrium constant has already been investigated by Dong et al. (Dong et al., 2010), thus we directly exploited their results. Finally, for reaction r_6, parameters for Keq according to expression (11) have been calculated based on experimental data by (Li et al., 2017) reporting the amine protonation constant at different temperatures.

2.4 Theoretical background of activity-based VLE models

A thermodynamic VLE model is essential to define interactions between the constituents of a mixture under vapour-liquid equilibrium conditions. The selection of the most suitable model is strongly dependent on the specific system under investigation. Amine-based solvents are characterized by a strongly non-ideal liquid phase behavior, mainly due to the formation of several interacting cationic and anionic species. Conversely, the interactions in the gas phase can be neglected (i.e., ideal gas behavior and ideal gas mixture) unless the system is highly pressurized (P > 10 bar). The cation-anions interactions are negligible as well in the gas phase since charged molecules do not vaporize. Under these assumptions, the gas phase can be assumed close to ideal conditions, thus, a cubic equation of state, or even, the ideal gas models, are suitable for characterizing the vapor phase in equilibrium with its liquid mixture. Binary interactions in the liquid phase for a strongly non-ideal system, such as CO_2, can be adequately described through the so-called Non-Random-Two-Liquid (NRTL) model.

2.4.1 Chemical and phase equilibria

Chemical and phase equilibria model involves solving both chemical equilibria of the reactions in the liquid phase, as well as the multi-component phase equilibria. Amine systems involve both molecular species and a range of ionic species, which can make the numerical solution complex. The description of chemical reactions occurring in the system under investigation is described in section 2.3. In addition to the reaction speciation in the liquid phase, the vapor-liquid equilibria must be solved through the fundamental equilibrium criterion, which minimizes the Gibbs energy of the solution at phase equilibrium. Phase equilibrium is reached as the chemical potential (μ) of a certain species is equal in both phases (see equation (14)). Since the chemical potential can be directly linked to fugacity according to expression (15), the equilibrium can also be expressed by the equality of the fugacities (f) in the liquid and vapur phase. As a result, vapor-liquid equilibrium of a particular species i can be defined according to expression (16), when the Poynting correction factor and the non-idealities in the gas-phase are disregarded. Models based on expression (16) are called activity coefficient models since γ_i is the correction factor that is introduced to account for the molecular and cationic-anionic interactions occurring in the system.

$$\mu_i^{vap} = \mu_i^{liq} \quad (14)$$

$$d\left(\mathrm{n}\, f_i\right) = \frac{d\mu}{RT} \quad (15)$$

$$P \cdot y_i = \alpha \cdot x_i \cdot \gamma_i \quad (16)$$

Where the parameter α is defined in different ways according to the single species. It corresponds to the Henry (H_i) coefficients for the CO_2 since it is highly diluted in the liquid phase, whereas it is the vapor pressure for all the other species that can be present in the gas phase (amines and water). For the gas phase the ideal gas behavior has been adopted since the estimates of the critical properties and Pizter factor may contain large deviations affecting the predictions for the cubic equation of state. Since the equilibrium is reached at a given temperature and pressure, when the Gibbs free energy of the system is minimized, the optimal set of activity coefficients to characterize the liquid phase composition is calculated numerically by minimization following chosen reference states. When all activity coefficients approach the unity, it means that the system behaves as an ideal mixture. The higher the deviation of the system from ideality, the furthest from unity are the corresponding activity coefficient values. An adequate estimation of the activity coefficients (γ_i) is essential to define the composition of the liquid (including the forming cations and ions) in chemical and physical (global) equilibrium with the corresponding gaseous phase.

2.4.2 The e-NRTL activity coefficient model

The NRTL model is an activity coefficient model that correlates the activity coefficients of a compound with its mole fractions in the liquid phase (Renon and Prausnitz, 1969, 1968). It is based on the hypothesis of Wilson that the local concentration around a molecule is different from the bulk concentration, which is caused by a difference between the interaction energy of the central molecule with the molecules of its own kind and that with the molecules of the other components that are present in the system. The energy difference also introduces a non-randomness at the local molecular level, which is expressed by the parameter called non-randomness factor α.

The general expression of the NRTL model for determining the activity coefficient γ_i of the i-th generic species in a multicomponent mixture of *n* components is reported in the expressions (17) to (19) here below (Renon and Prausnitz, 1969, 1968), where τ_{ij} are the temperature-dependent parameters describing the interaction between a molecule or the ion i with another molecule or the ion j and α_{ij} is the non-randomness factor associated to the interaction of component i with component j. By definition, α_{ij} is symmetric, meaning that α_{ij} is equal to α_{ji}.

$$\ln(\gamma_i) = \frac{\sum_{j=1}^{n} x_j \cdot \tau_{ji} \cdot G_{ji}}{\sum_{k=1}^{n} x_k \cdot G_{ki}} + \sum_{j=1}^{n} \frac{x_j \cdot G_{ij}}{\sum_{k=1}^{n} x_k \cdot G_{kj}} \cdot \left(\tau_{ij} - \frac{\sum_{m=1}^{n} x_m \cdot \tau_{mj} \cdot G_{mj}}{\sum_{k=1}^{n} x_k \cdot G_{kj}} \right) \quad (17)$$

$$G_{ji} = \exp(-\alpha_{ij} \cdot \tau_{ij}) \quad (18)$$

$$\tau_{ij} = A_{ij} + \frac{B_{ij}}{T} \quad (19)$$

The NRTL method has been extended to account for cation-anion pairs with neutral molecules inside mixed solvent electrolyte systems in a wide temperature range (Chen and Song, 2004; Hartono et al., 2021; Lin et al., 2022). The ELECNRTL model is based on the same theoretical framework as the generic NRTL model, but the expression is modified compared to the original Renon and Prausnitz NRTL model. This modification introduces the like-ion repulsion and local electroneutrality assumptions (Lin et al., 2010) to provide a more representative picture of the electrical charge effects, which play a key role in amine solutions. The resulting model succeeds in characterizing both short- and long-range interactions in the presence of electrical charges utilizing additional interaction parameters.

The excess Gibbs free energy (G^E) NRTL expression modified for electrolyte systems is reported in the equation (20), where *m* stands for the generic neutral molecular species, *c* for cations, and *a* for anions. The

X_i (capital X) is defined in expression (21) as the product of the molar fraction of the generic species *i* (x_i) times a coefficient C_i which is assumed equal to unity for neutral molecules and to the absolute value of the charge for the ions (Lin et al., 2010). We remark that expressions (18) and (19) of the general NRTL model are still valid for electrolyte systems, and the parameters A_{ij} and B_{ij} in the equation (19) are called GMELCC and GMELCD parameters in Aspen Plus, respectively. The latter ones define the temperature dependence for anion/cation - molecule pairs interactions.

$$\frac{G^E}{RT} = \sum_m X_m \cdot \frac{\sum_j X_m \cdot G_{jm} \cdot \tau_{jm}}{\sum_k X_k \cdot G_{jk}} + \sum_c X_c \cdot \sum_{a'} \frac{X_{a'} \cdot \sum_j G_{jc,a'c} \cdot \tau_{jc,a'c}}{(\sum_{a''} X_{a''}) \cdot \sum_k X_k \cdot G_{kc,a'c}} + \sum_a X_a \cdot \sum_{c'} \frac{X_{c'} \cdot \sum_j G_{ja,c'a} \cdot \tau_{ja,c'a}}{(\sum_{c''} X_{c''}) \cdot \sum_k X_k \cdot G_{ka,c'a}} \quad (20)$$

$$X_i = x_i \cdot C_i \quad (21)$$

2.4.3 System speciation

Differently from soft models, which typically deal only with neutral molecules (amines, water and CO_2) and cannot distinguish between an amine and its protonated form, the ELECNRTL model is a true composition model since it is able to fully describe the composition of the system in the liquid phase including the single cationic and ionic species, the so-called speciation. The characterization of the liquid composition is provided by means of reaction equilibrium constants and the activity coefficients (see section 2.4.1). Such an increased level of detail allows a better understanding of the system, in particular the estimation of the relative content of bicarbonate and carbamate, which are forming as a result of two competitive reactions, and the thermodynamic behavior in solution (Richner and Puxty, 2012). Furthermore, by monitoring the speciation in CO_2 absorption/desorption processes, information on amine structure relationships, reaction mechanisms, influences of process operating conditions, and a deeper understanding of the absorption kinetics of the blend can be gathered (Perinu et al., 2018).

For chemical absorption of CO_2 by aqueous amine solvents, the most widely adopted technique to identify and quantify the species formed as a result of interactions between the unloaded solution and CO_2 is NMR spectroscopy (Chen et al., 2022). For the HS3 blend, no speciation data have been collected so far, meaning that a direct comparison between experimental liquid speciation and liquid speciation predicted by the VLE model is not possible. Anyway, the HS3 speciation as predicted by the new ELECNRTL model is presented in section 3.7 together with a list of considerations based on the published literature on AP and PRLD and in-house absorption heat data for HS3 that justify the observed behavior, at least from a qualitative point of view.

2.5 Physical properties

A proper carbon capture process design requires the characterization of the fluidodynamics of the reacting systems, the correct estimation of the CO_2 capture plant energy requirements as well as the kinetics of absorption and desorption (Guo et al., 2019). Physical properties such as density, viscosity and heat capacity of both pure components and their blend have a not negligible influence. More specifically, some authors remark that the liquid-film coefficients for mass transfer and vapor liquid equilibrium depend on the solution density, viscosity, and surface tension. In turn, this influences also the mass transfer rates inside both the

absorber and the regenerator (Balchandani et al., 2022). Additionally, the pumping costs associated with amine solvent are significantly influenced by the viscosity of the solvents. Finally, an incorrect estimate of the amine heat capacities directly results in a inaccurate estimation of the contribution to the reboiler duty given by the sensible heat required to heat the rich-solvent up to the bottom reboiler temperature. For all these reasons, it is fundamental to properly fix density, viscosity and specific heat of all the molecules involved in the system before proceeding with the regression of the VLE interaction parameters.

Aspen Plus V11.0 allows fitting temperature dependent density, viscosity and heat capacity models for pure component and both temperature and loading-dependent expressions based on dedicated mixing rules to characterise amine-water mixtures (Aspen Plus®, 2019). In this work, liteature data have been exploited to regress dedicated density, viscosity and specific heat polynomials for pure AP and PRLD (Hartono and Knuutia, 2023; Idris and Eimer, 2016; Idris et al., 2018; Mundhwa and Henni, A., 2007). Moreover, density and viscosity observations for AP-water and PRLD-water solutions at different temperatures and progressively increasing amine concentrations have been exploited to characterize amine densities and viscosities at different molarities.

The density, viscosity and specific heat models obtained in this work and a comparison between the model prediction and the corresponding experimental data are described in the Supplementary Material.

2.6 General methodology to regress NRTL and ELECNRTL coefficients

2.6.1 NRTL VLE model: molecule-molecule interaction parameters

Before moving to the definition and estimation of the ELECNRTL coefficients, it is important to fix the equilibrium parameters for the uncharged blend, namely the equilibrium condition in the absence of CO_2. Since the CO_2 is not dissolved into the solvent and no charged molecules are generated (except for water self-ionization), the molecule-molecule interactions are the most relevant to describe the phase equilibria established between the liquid and corresponding vapour. In general, the PRLD-H_2O and AP-H_2O interaction parameters should be regressed using Aspen Plus V11 Regression toolbox with the "maximum likelihood" algorithm starting from binary VLE experimental data. The regression is repeated using each time as a guess value for the results of the previous iteration until the difference between two consecutive iterations is lower than 0.1% for each parameter. The aim of this iterative procedure is to find the global optimum instead of just a local minimum of the Sum of Square Errors (SSE) between each experimental datum and its model predictionIn case of no or a few experimental data may be available for the amine-water system,it is worth observing that the amine-water system equilibria are also present when CO_2 is dissolved. Thus, the amine-CO_2-H_2O data can be used to get the NRTL coefficients as well.

For what concerns specifically the HS3 blend, the NRTL parameters had already been fitted on PRLD-H_2O VLE data by Bernhardsen (Bernhardsen et al., 2019) and on AP-H2O data by Bunevska (Bunevska, 2021). No parameters accounting for AP-PRLD interactions have been considered since amine-amine interactions can be neglected to increase the model robustness in accordance with all the other template ELECNRTL models for amine blends proposed by AspenTach (Aspen Plus®, 2019). Amine-amine-water interaction parameters could be regressed if blend-water equilibria data for unloaded solution are available. However, this kind of data was not available for this system.

2.6.2 ELECNRTL VLE model: ion-molecule interaction parameters

The ELECNRTL package accounts for both long- and short-range interactions among molecules and pairs of cations and anions. The electrostatic interactions are relevant in the liquid phase since the physical

entanglement between the different charged and uncharged molecules affects the activity of each species. The regression of the ion-molecule interaction parameters has been carried out using experimental measurements of the CO_2 partial pressure (PCO_2) at different loading [mol_{CO2}/mol_{amine}] data for the HS3 blend, which is a quaternary system (AP-PRLD-H_2O-CO_2). In principle, AP-H_2O molecule-ion intercation coefficients should be regressed starting from ternary AP-H_2O-CO_2 VLE data and the corresponding PRLD-H_2O interaction from ternary VLE-H_2O-CO_2 data, while quaternary data should be used only to tune the AP-PRLD molecule-ions interactions. This procedure would lead to a general model, valid for whatever relative content of AP, PRLD and H_2O. Despite the advantage of getting a general model, this could lead to significantly higher errors in the VLE prediction at the specific HS3 solvent composition. Since the main aim of this work is the development of an accurate model to represent the HS3 solvent, the fitting has been done directly using only quaternary HS3 data. This lead to a more accurate and reliable model for the considered blend. On the other hand, there is no reliability in extrapolating the model for other amine concentration, which is underlined as a limitation.

The general approach described in this section aims at providing a standard procedure to regress the ELECNRTL parameters by reducing their amount to shorten and speed up calculations. The latter feature is crucial since many regressed parameters guarantee numerical accuracy, whereas it may lead to convergence issues when simulating an entire distillation/absorption column due to heavy computational efforts and high potential correlation among the ELECNRTL parameters. Thus, a balanced trade-off between accuracy and the number of parameters is required. The interaction parameters are classified in temperature non-dependent parameters, denoted in Aspen Plus as GMELCC, corresponding to A_{ij} in Equation (19), and temperature-dependent parameters, corresponding to GMELCD in Aspen and B_{ij} in Equation (19). To make the system as simple as possible, it is worth looking first into the GMELCC, disregarding any temperature dependence. The temperature dependence can be investigated separately. The best algorithm for the regression of the ELECNRTL is the "maximum likelihood" (ML), which minimizes the gap between experimental observations and model predictions changing the GMELCC (and GMELCD) parameters without fixing any variable (temperature, pressure, liquid, and vapor composition). In other words, a multi-dimensional minimization problem is solved. The experimental dataset should cover the entire range of temperatures and loading for the domain of interest.

The complete procedure to regress the ELECNRTL parameter is here described:

1. As the first attempt, only the GMELCC (A_{ij}) are considered for the regression, and they are initially set equal to their default values (Britt et al., 1982; Mouhoubi et al., 2020) ($A_{CO2,ca}$=15, $A_{ca,CO2}$= −8, $A_{amine,ca}$= 8, $A_{ca,amine}$= −4, $A_{H2O,ca}$= 8, $A_{ca,H2O}$= −4, where *c* and *a* stand for a generic cation and anion, respectively). To simplify the system, all the interactions of CO_2 as molecular species with the carbamate and the two protonated amines are set equal to zero. Moreover, due to their low concentration (thus, negligible molar fraction), any GMELCC parameters accounting for any interaction with H_3O^+ as cation or OH^- and CO_3^{--}as anion are not included in the regression procedure and they are fixed to the corresponding default value when describing the interactions with water and equal to zero for the interactions with the two amines. The proposed assumption is acceptable since the molar fraction of H_3O^+ as cation or OH^- and $CO3^{--}$species is very low in amine systems, meaning that their impact on the activity coefficients in equation (20) is negligible (Frailie et al., 2011; Li et al., 2014). The VLE model developed for HS3 confirms this assumption, since the predicted mole fractions of the three mentioned ions ranges 10^{-4} – 10^{-9}. As a matter of fact, these species are diluted into the solvent and, according to the NRTL model, the activity coefficient $\gamma_i \rightarrow 1$ (ideal liquid condition) and the VLE conditions are described by the Raoult model.The remaining GMELCC are then regressed with the ML algorithm.
2. The regression procedure is repeated several times to try to ensure that a real optimum was found instead of just a local minimum. More in detail, the regression procedure is repeated until further iterative steps would result in negligible changes of all interaction parameters with respect to the

previous iteration (maximum relative discrepancy of 5% is accepted as a threshold). The resulting required number of iterations according to the mentioned criterion is 10. The results of each iteration are exploited as new guess starting values for the following one. The set of parameters with minimum square error and variance of the GMELCC is considered the optimal solution.

3. To improve the prediction capacity of the ELECNRTL model at high temperature, it is possible to include the GMELCD (B_{ij}) parameters which account for the temperature effect. Before starting, all the GMELCD to be regressed are set equal to zero (default value), and the GMELCC coefficients have been also reset to their default values.In the current work, we considered all the possible GMELCD parameters with a corresponding GMELCC regressed at point [1]. In other words, GMELCD considering H_3O^+ as cation or OH^- and CO_3^{--} as anion in combination with the two amines were still disregarded.
4. To avoid overfitting and a vast number of ELECNRTL parameters, all GMELCD < 50.0 (in absolute value) after three iterations have been removed and fixed to zero.
5. Before the last regression, the remaining GMELCC and GMELCD parameters were reset to their default values. The ML algorithm has been applied ten times, and the solution showing the minimum sum of errors and variance has been chosen as the best.

Once the final model has been obtained, a point-to-point evaluation analysis using Aspen Plus V11 regression tool (in estimation mode) with the "ordinary least square" (OLS) algorithm has been performed to verify the experimental data matching and the accuracy of the model. This algorithm calculates the model prediction in terms of total pressure and vapour phase composition at fixed temperature and liquid composition. The statistical indicators, the average Relative Error (RE) and Average Absolute Error (AE) are are used to assess the accuracy and the precision of the model. The accuracy is referred to the ability of a model to lie close to the experimental points, and the index of this feature is RE. The precision is related to the dispersion of the model and how much the results are distributed around the experimental observations (i.e., the precision of the model). The AE directly estimates this. The mean relative error (RE) is calculated according to Equation (22), where *z* stands for the variable on which the error is calculated (for example the pressure and molar fraction of water and PRLD in the vapor phase), *i* stands for the generic experimental point and *n* for the total number of measurements.

$$\mathrm{RE} = \frac{1}{\mathrm{n}} \cdot \sum_{\mathrm{I}=1}^{\mathrm{n}} \left| \frac{\mathrm{z_{i,exp}} - \mathrm{z_{i,mod}}}{\mathrm{z_{i,exp}}} \right| \tag{22}$$

The overall absolute error (AE) is instead defined according to Equation (23):

$$AE = \sqrt{\sum_{\mathrm{i}=1}^{\mathrm{n}} \frac{\left(\mathrm{z_{i,exp}} - \mathrm{z_{i,mod}}\right)^2}{\mathrm{n}}} \tag{23}$$

It is remarkable that for an amine blend the maximum number of possible ELECNRTL parameters is

$$\frac{3\mathrm{n_M}!}{\mathrm{n_M} - 2} + 5\mathrm{n_M n_C n_A} \tag{24}$$

where n_M, n_C, and n_A are the number of molecules, cations, and anions, respectively. Thus, for an amine blend made up of a primary amine and a tertiary amine, it is possible to define up to 276 coefficients (considering both GMELCC and GMELCD and neglecting pair cation-anion interactions). Such a high number of parameters results in overfitting and could lead to high correlation among the parameters. The suggested numerical procedure reduces by almost 88% the number of ELECNRTL regressed coefficients without appreciable loss

in accuracy. For instance, for the HS3 blend, we defined globally 34 ELECNRTL parameters subdivided into 24 GMELCC and 10 GMELCD. Thus, the proposed approach intrinsically helps define a codified procedure reducing the number of parameters and focusing on the most relevant parameters.

2.7 CO2SIM soft model (comparative model)

Finally, we compared the VLE equilibrium results from the ELECNRTL model implemented in Aspen Plus V11 with the ones obtained from CO2SIM, for the specific blend. CO2SIM is a standalone software developed in SINTEF Industry – Process Technology department to generate and simulate amine-based capture plants. The CO2SIM software has been successfully implemented and validated over several pure amine and amine blends (Lindqvist et al., 2014; Majeed and Svendsen, 2018; Pinto et al., 2014; Tobiesen et al., 2018, 2008, 2007). Differently from the Aspen Plus suite, CO2SIM for this particular solvent describes the VLE adopting soft model approach (Brúder et al., 2012), in a so-called non-rigorous manner. In CO2SIM's chosen soft equilibrium model, the partial pressure of the CO_2 in the gas phase (P_{CO2}) in equilibrium with the liquid solvent is defined as a function of the solvent loading (α) and temperature. The soft model structure has been largely discussed and presented in previously cited works. Concerning the general structure, the soft model has some adaptative coefficients (k-parameters, B, and C) which are fitted to the experimental data for an assigned blend:

$$\ln\left(\mathrm{P_{CO_2}[kPa]}\right) = \mathrm{B}\cdot\ln(\alpha) + \mathrm{A_1} + \frac{\mathrm{C}}{1 + \mathrm{A_2}\cdot\exp[-\mathrm{A_3}\cdot\ln(\alpha)]} \quad (25)$$

Despite the absence of a true thermodynamic framework, the soft model ensures good accuracy without any numerical effort. Although speciation models are available in CO2SIM, the main advantage of the much used soft models lies in the possibility to easily get fast calculations and to catch the main dependence of the dependent variable (i.e., the partial pressure of free CO_2 in the gas phase) just considering the main system variables as the solution loading and the temperature. Thus, the soft VLE model is empirically based on a loading- and temperature-dependent terms, and it represents a smart short-cut for a fast representation of experimental VLE data and interpretation of the amine/blend performance. The limited validity range (i.e., unfeasible extrapolation of the model outside the regression domain) represents the main drawback of the soft model. Moreover, this soft model defines the HS3 as a pseudo component, thus, it is not able to distinguish between the two single amine constituents. These limitations are related to the absence of a real phenomenological and physics-based model, like the ELECNRTL theory.

2.8 Heat of absorption

The reaction between CO_2 and an amine solution is an exothermic process, thus it is associated with the release of a certain quantity of heat, resulting in a system temperature increase. The amount of heat released during the CO_2 absorption process is called the heat of absorption. This thermal energy depends on the solvent formulation, the CO_2 loading and the temperature. A correct estimation of the heat of absorption for acid gases (mainly CO_2 and H_2S) in aqueous amines solutions is of prime importance for designing unit operations of acid gas removal, because it directly affects the steam requirements associated with amine regeneration and its connection to the temperature dependency of the CO_2 equilibrium (Kim and Svendsen, 2011). On the one hand it is advisable to keep the absorption enthalpy as low as possible, as the steam cost often accounts for over half the operating cost of the plant. On the other hand, this may negatively affect the capture performance within the absorber. Even if the temperature dependency of the heat of absorption is sometimes neglected assuming a constant value both for absorber and desorber conditions (Kohl and Nielsen, 1997), experimental observations show that differences between the reaction heat estimate at 40°C

and at 120°C can reach 25–30% (Kim and Svendsen, 2011). Furthermore, accounting also for the dependency on the loading can lead to improvements in the correct optimal design of a CO_2 capture facility. Based on these considerations, it is essential for models to be implemented in process simulators to correctly predict absorption heat in the whole temperature and loading ranges of interest in order to guarantee a reasonable estimation of the energy requirements of the CO_2 capture plant and, as a consequence, of the operating costs.

The absorption heat associated with the reaction between CO_2 and the HS3 blend has been determined in a temperature range between 40°C and 100°C and in a CO_2 loading range between 0.03 and 0.81 employing a reaction calorimeter (Hartono et al.).

In this work, the available experimental observations for the primary and tertiary amine protonation heat and carbamate formation have been used to tune the Aspen ELECNRTL model to get an accurate estimation of the HS3 absorption heat. A comparison between the experimental data and the resulting model prediction is shown in section 3.8 to verify the reliability of the new proposed model. The following sub-paragraph provides an overview of the theoretical framework followed by Aspen Plus to estimate the reaction heat starting from the enthalpy of formation and the ideal gas, liquid, and diluted aqueous phase heat capacities of each molecular and ionic species involved in the reacting system. This section also describes the procedure that can be followed to estimate enthalpy of formation or heat capacity data for which no experimental observations are available, starting from the heat of absorption data. The proposed approach is applicable for the characterization of absorption heat in whatever blend.

2.8.1 Enthalpy calculations in Aspen Plus

In a default ELECNRTL package, the enthalpy of a particular species at a given temperature (T) is calculated according to expression (26) for a neutral molecule ($H_{molecule}$) and according to expression (27) for ions (H_{ion}), where the liquid (cP_{liq}) and aqueous (cP_{aq}) heat capacities are defined as a function of the temperature through expressions (28) and (29), respectively.

$$\mathrm{H_{molecule}(T)} = \Delta \mathrm{H^{0}_{f\ gas}(298.15K)} - \Delta \mathrm{H_{ev}(298.15K)} + \int_{298.15\ \mathrm{K}}^{\mathrm{T}} \mathrm{cP_{liq}} \cdot \mathrm{dT} \tag{26}$$

$$\mathrm{H_{ion}(T)} = \Delta \mathrm{H_{f\,aq}{}^{0}(298.15K)} + \int_{298.15\ \mathrm{K}}^{\mathrm{T}} \mathrm{cp_{aqueous}dT} \tag{27}$$

$$\mathrm{cP_{liq}} = \mathrm{A} + \mathrm{B} \cdot \mathrm{T} + \mathrm{CT^2} + \mathrm{D} \cdot \mathrm{T^3} + \frac{\mathrm{E}}{\mathrm{T^2}} \tag{28}$$

$$\mathrm{cP_{aq}} = \mathrm{A} + \mathrm{B} \cdot \mathrm{T} \tag{29}$$

In absence of specific calorimetric data on ionic species heat capacity, the aqueous heat capacity of protonated amines can be set equal to the corresponding pure amine liquid heat capacity to simplify calculations. Pure amines liquid heat capacities have been fitted to published experimental data for both AP and PRLD (see Supplementary Material). The ideal gas enthalpy of formation of CO_2 and H_2O as well as the aqueous enthalpy of formation of CO_3^{--}, HCO_3^{-}, H_3O^{+} and OH^{-} are available in the Aspen database and have been used successfully to characterize many amine systems (Aspen Plus®, 2019). Therefore, the only unknown parameters in expressions (26) to (29) are the enthalpies of the formation of pure and protonated AP and PRLD as well as the carbamate formation enthalpy. The formation enthalpy of AP and PRLD can be approximately estimated by means of Gani group contribution method (Constantinou and Gani, 1994). The

estimated values are comparable to those reported in the MEA-MDEA Aspen Plus V11.0 framework. The remaining formation enthalpies of APH^+, $APCOO^-$ and $PRLDH^+$ can be regressed from absorption heat data at a fixed temperature (no loading dependence). Considering the definition of reaction heat reported in expression (30), where θ is the stoichiometric coefficient, a minimization problem is solved to calculate the optimal $\Delta H_f^0, APH^+$ from the AP protonation (r_4) reaction heat (Bunevska, 2021), $\Delta H_f^0, APHCOO^-$ and $\Delta H_f^0, PRLDH^+$ from global CO_2 absorption reactions (31) and (32), respectively, starting from in-house absorption heat data determined for pure AP and pure PRLD-based solvents, respectively.

$$\Delta H^R(T) = \sum_{i=1}^{N_{products}} \Delta H_f^0, i(T) \cdot \vartheta_i - \sum_{j=1}^{N_{reactants}} \Delta H_f^0, j(T) \cdot \vartheta_j \quad (30)$$

$$\mathrm{AP} + \mathrm{CO_2} \rightleftharpoons \mathrm{APH^+} + APCOO^- \quad (31)$$

$$\mathrm{PRLD} + \mathrm{H_2O} + \mathrm{CO_2} \rightleftharpoons \mathrm{PRLDH^+} + HCO_3^- \quad (32)$$

3 RESULTS AND DISCUSSION

In this section, we present the results obtained by applying the guidelines proposed in the Methods paragraph.

3.1 Henry constants

Table 2 lists the values of parameters A, B, C and D for the Henry constant (He) of CO_2 in both pure amines as in Equation (2). Their values result from the minimization of the relative square deviations between the solubility calculated based on the experimental solubility data and the model predictions. Figure 2 shows the graphical comparison of the CO_2 solubility data rescaled according to the N_2O solubility analogy. The model proves accurate in the whole temperature range of interest and the model has a reasonable shape also at high temperatures where there is no experimental data available.

Table 2. Henry law constant coefficients defining CO_2 physical solubility in AP and PRLD regressed in this work.

Parameter	CO_2 - AP	CO_2 - PRLD
A	-54.6317	10.9911
B	-2.0334	0.3802
C	12.1097	-1.1906
D	-0.0213	0.0130

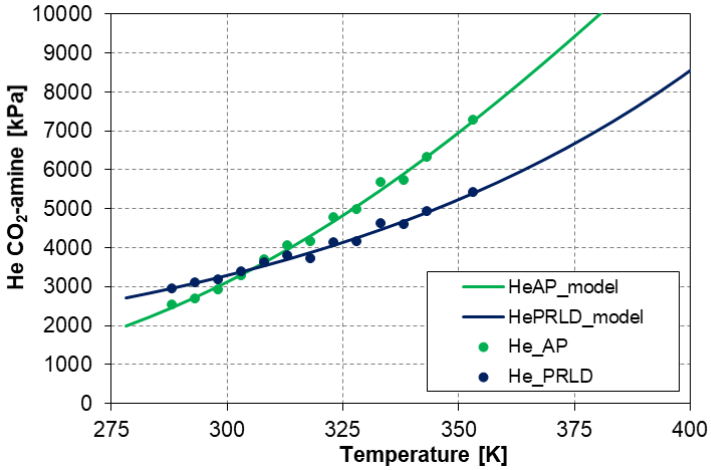


Figure 2. Henry law constant defining CO_2 physical solubility in AP and PRLD: model (solid line) and experimental data (dots).

3.2 Vapor pressure

Antoine equation parameters C_1, C_2 and C_3 (refer to Equation (4)) are already available in the literature for AP (Green and Perry, 2007), but they have been refitted in order to get an expression where coefficients are compliant with the unit of measure implemented in Aspen Plus and reported in Equation (4). Conversely, the coefficients of the PRLD have been fitted in this work to the vapor pressure data collected in Berhardsen (Bernhardsen et al., 2019). A sum of relative square errors of only 0.7% is obtained. Antoine equation parameters regressed in this contribution and a comparison between the experimental PRLD vapor pressure data collected in the literature and the model prediction are provided in Table 3 and Figure 3, respectively.

Table 3. Antoine coefficients for AP and PRLD vapor pressures fitted (vapor pressure in [bar] and temperature in [K]).

Parameter	AP	PRLD
C_1	11.9628	20.3877
C_2	-4482.90	-12733.55
C_3	-85.50	171.53

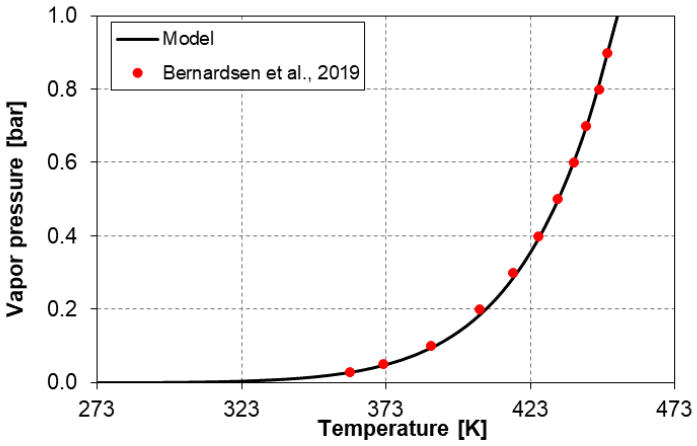


Figure 3. PRLD vapor pressure: experimental data (Bernhardsen et al., 2019) **and predictions using Antoine model.**

3.3 Equilibrium constants of the elementary reactions scheme

The equilibrium constants for the elementary reactions (5) - (10) have been taken from the literature. For the AP protonation and AP global reaction with CO_2 (expressions (8) and (9)), Dong et al. (Dong et al., 2010) provided a loading-dependent equilibrium constant expression. This has been reformulated and regressed into the Aspen Plus complaint form reported in Equation (11). Table 4 lists the coefficients for equilibrium constants of the elementary reactions adopted to describe the CO_2 capture using the HS3 blend as solvent.

Table 4. Coefficients for molar fraction-based equilibrium constants according to expression (11).

	r_1 Equation (5)	r_2 Equation (6)	r_3 Equation (7)	r_4 Equation (8)	r_5 Equation (9)	r_6 Equation (10)
A	132.899	231.465	216.049	-106.105	1.21526	-10.4165
B	-13445.9	-12092.1	-12431.7	-4134.2	-1068.67	-4234.98
C	-22.4773	-36.7816	-35.4819	16.2313	-	-
D	-	-	-		-	-
Source	(Posey and Rochelle, 1997)	(Posey and Rochelle, 1997)	(Posey and Rochelle, 1997)	Refitted from Dong (Dong et al., 2010)	Refitted from Dong (Dong et al., 2010) and Rochelle (Posey and Rochelle, 1997)	Calculated from Li et al., 2017

3.4 NRTL model coefficients (molecule-molecule interactions

514 Table 5 gathers the NRTL coefficients for the H_2O-AP and H_2O-PRLD interactions as available in the literature.

515

516 **Table 5. NRTL parameters implemented in Aspen Plus for the molecule - molecule interactions**

Aspen Plus NRTL coefficient	Parameters in expressions (18) and (19)	Component i	Component j	Value (SI units)	Source of experimental values
NRTL/1	A_{ij}	H_2O	AP	5.3843	(Bunevska, 2021)
NRTL/2	B_{ij}	H_2O	AP	-0.9199	
NRTL/1	A_{ji}	AP	H_2O	-989.213	
NRTL/2	B_{ji}	AP	H_2O	-440.101	
NRTL/3	$\alpha_{ij} = \alpha_{ji}$	H_2O	AP	0.2	
NRTL/1	A_{ij}	H_2O	PRLD	1.1755	(Bernhardsen et al., 2019)
NRTL/2	B_{ij}	H_2O	PRLD	-0.1156	
NRTL/1	A_{ji}	PRLD	H_2O	-1103.81	
NRTL/2	B_{ji}	PRLD	H_2O	1715.89	
NRTL/3	$\alpha_{ij} = \alpha_{ji}$	H_2O	PRLD	0.2	

517

518 ### 3.5 ELECNRTL model coefficients (molecule - anion/cation pairs interactions)

519 Table 6 gathers the values for the regressed ELECNRTL model (both GMELCC and GMELCD). The coefficients
520 missing in this list are set to their default values or to zero, as mentioned in the methodology proposed in
521 Section 2.6.2.

522

523

524 **Table 6. ELECNRTL coefficients (GMELCC and GMELCD) implemented in Aspen Plus to characterize pure amines and the HS3 blend.**
525 **The table reports only the coefficients which are not set to default values.**

ELECNRTL coefficient Aspen Plus name	Element i	Element j	Value (SI units)
GMELCC	H_2O	($PRLDH^+$,HCO_3^-)	13.6961
GMELCC	($PRLDH^+$,HCO_3^-)	H_2O	-5.4276
GMELCC	PRLD	($PRLDH^+$,HCO_3^-)	29.0442
GMELCC	($PRLDH^+$,HCO_3^-)	PRLD	8.7717
GMELCC	H_2O	(APH^+,HCO_3^-)	12.6182
GMELCC	(APH^+,HCO_3^-)	H_2O	-5.5317
GMELCC	H_2O	(APH^+,$APCOO^-$)	10.5229
GMELCC	(APH^+, $APCOO^-$)	H_2O	-6.9975
GMELCC	AP	(APH^+, HCO_3^-)	87.2557
GMELCC	(APH^+, HCO_3^-)	AP	60.3790
GMELCC	AP	(APH^+, $APCOO^-$)	20.7888
GMELCC	(APH^+, $APCOO^-$)	AP	34.8014
GMELCC	H_2O	($PRLDH^+$, $APCOO^-$)	10.9464
GMELCC	($PRLDH^+$, $APCOO^-$)	H_2O	-5.1289
GMELCC	AP	($PRLDH^+$, HCO_3^-)	52.3316
GMELCC	($PRLDH^+$, HCO_3^-)	AP	35.0286
GMELCC	AP	($PRLDH^+$, $APCOO^-$)	4.5923

GMELCC	($PRLDH^+$, $APCOO^-$)	AP	-1.3794
GMELCC	PRLD	($PRLDH^+$, $APCOO^-$)	12.5491
GMELCC	($PRLDH^+$, $APCOO^-$)	PRLD	2.8911
GMELCC	PRLD	(APH^+, HCO_3^-)	11.6230
GMELCC	(APH^+, HCO_3^-)	PRLD	0.1155
GMELCC	PRLD	(APH^+, $APCOO^-$)	7.4596
GMELCC	(APH^+, $APCOO^-$)	PRLD	19.9230
GMELCD	PRLD	($PRLDH^+$, HCO_3^-)	888.2463
GMELCD	($PRLDH^+$, HCO_3^-)	PRLD	8810.9267
GMELCD	AP	(APH^+, HCO_3^-)	1959.2531
GMELCD	(APH^+, HCO_3^-)	AP	1514.6851
GMELCD	AP	(APH^+, $APCOO^-$)	-259.7171
GMELCD	(APH^+, $APCOO^-$)	AP	432.8310
GMELCD	AP	($PRLDH^+$, $APCOO^-$)	530.2970
GMELCD	($PRLDH^+$, $APCOO^-$)	AP	-789.5392
GMELCD	PRLD	($PRLDH^+$, $APCOO^-$)	-2337.3930
GMELCD	($PRLDH^+$, $APCOO^-$)	PRLD	-66.6320

Finally, the authors performed a statistical analysis of the results over the different datasets we used for the regression of the ELECNRTL coefficients. Table 7 resumes the performance of the regression for the data clusters. The statistical analysis neglects the amines partial pressure due to its low numerical value which is not relevant to the present discussion. Thus, the error analysis is limited to CO_2 and water vapor partial pressure, which represent the main components present in the vapor phase. Overall, the statistical analysis shows good accuracy and precision of the model, since the average relative errors are below 20% and the absolute deviations are close to 7 kPa. Such results confirm the reliability of the regression procedure presented in this contribution. The largest deviations are registered for the predictions of the CO_2 partial pressure data. These deviations are enhanced by the fact that a significant number of experimental data report a very low measured partial pressure of CO_2. Thus, even though the absolute value may be close to the experimental one (as shown by looking at the average AE), the relative error increases. For this reason, the relative error on CO_2 partial pressure calculated accounting only for the data associated with a CO_2 partial pressure higher than 1 kPa is also included in the statistical analysis. The results demonstrate that it is possible to build up an ELECNRTL model from scratch even though one or more components making up the blend are missing in the defaults Aspen Plus database.

Table 7. Average AE and RE of CO_2 and water partial pressure predictions for the ELECNRTL and CO2SIM models for HS3 developed in this work and corresponding experimental data available in the literature for the AP-PRLD-H_2O-CO_2 system (HS3 blend).

			RE [%] as in Equation (22)		**AE [bar] as in Equation** (23)	
Model	**Data source**	**Chart (P_{CO2} vs loading)**	**P_{CO2}**	**P_{H2O}**	**P_{CO2}**	**P_{H2O}**
ELECNRTL	Hartono et al.	Figure 4	17.84	17.00	0.0712	0.0705
ELECNRTL	Hartono et al. only data with P_{CO2} > 1 kPa	Figure 4	14.81	-	-	-
CO2SIM	Hartono et al.	Figure S8 and S9	14.29	-	0.214	-

Figure 4 depicts the VLE curves for the HS3 blend over different loading at different temperatures, which are the most relevant for CCS plant. The Aspen Plus ELECNRTL model shows good accuracy in representing the equilibrium conditions in the whole temperature (40°C-120°C) and loading (0.1 – 0.5) range of interest for both absorption and solvent regeneration (Dutcher et al., 2015; Liu et al., 2016; Mangalapally and Hasse, 2011; Rao and Rubin, 2002; Rochelle, 2009). Moreover, it is possible to claim that the model can be extrapolated since the profiles are smooth and no abnormal trends are registered. For a comparison between ELECNRTL model and the soft model developed in CO2SIM, please refer to the following paragraph.

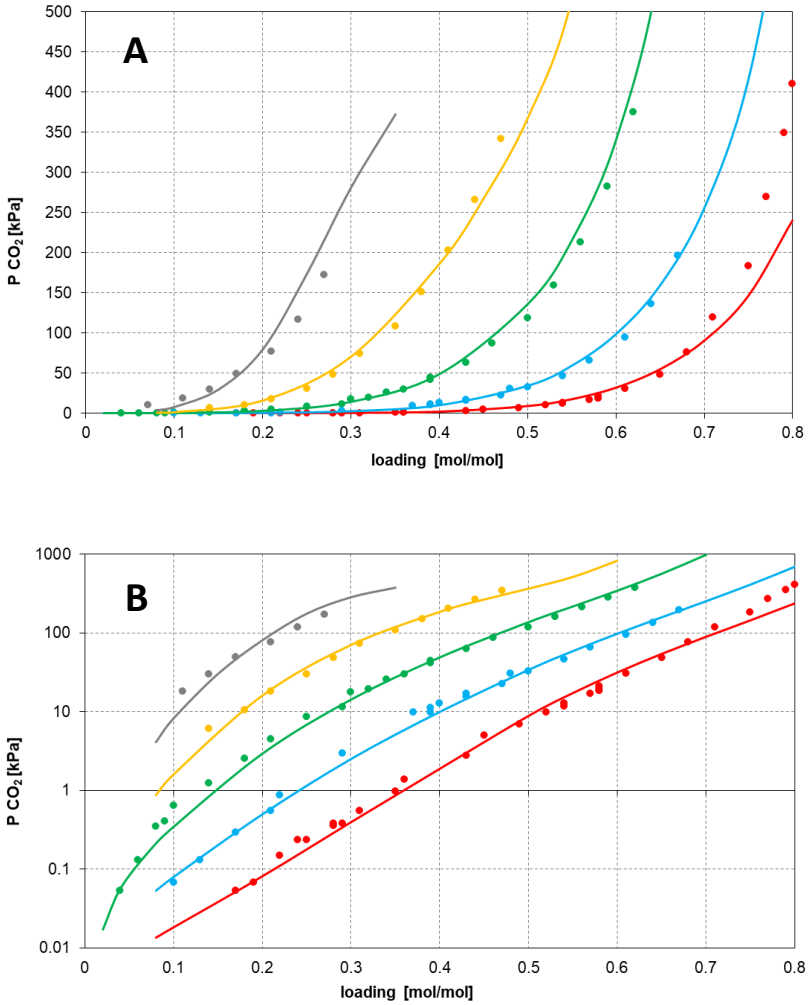


Figure 4. Comparison between the ELECNRTL model predictions (solid lines) and the experimental data (dots) for the HS3 blend at different temperatures: 40°C (red), 60°C (light blue), 80°C (green), 100°C (yellow), and 120°C (grey). The plot is proposed both in normal scale (A - top) and logarithmic (B - bottom). Data by Hartono (Hartono et al.).

3.6 Comparison of the Aspen Plus ELECNRTL model with the CO2SIM soft model

We compared the ELECNRTL model with the soft model implemented in the in-house CO2SIM process simulator. The necessity to verify the reliability of the ELECNRTL model drives the choice of comparing two different models, one theory-based (Aspen ELECNRTL) and one empirical (CO2SIM soft model). We considered the CO2SIM model as a benchmark since previous works (Brúder et al., 2011) proved that CO2SIM soft model represents accuracately and with precision amine(s) VLE as already mentioned in Section 2.7. The coefficients of the empirical CO2SIM soft VLE model have been regressed to define the CO_2 partial pressure's dependency on loading and temperature for the HS3 blend allowing a comparison of two models for the HS3

blend. A graphical comparison between the ELECNRTL and the CO2SIM model can be found in the Supplementary Material. The ELECNRTL model is associated with a slightly higher relative error but also with (Brúder et al., 2011)a significantly lower (-66%) absolute error (Table 7). This result is in someway expected, considering that the algorithm exploited for the regression procedure in Aspen Plus V11.0 is based on the minimization of the absolute deviations between the experimental data and the model prediction. The CO2SIM soft VLE model looks smoother, but only the Aspen ELECNRTL model can differentiate between the two amine constituents (AP and PRLD), while the soft model deals with a pseudo component including both amines together. Therefore, under proper validation with additional experimental data, the Aspen ELECNRTL model can be extended to describe not only the specific HS3 blend composition but also whatever solvent composition between pure ternary AP-H_2O-CO_2 and pure PRLD-H_2O-CO_2 systems. Finally, conversely to the soft model, which does not take into account the formation of cations and anions in the system, the ELECNRTL model provides details concerning the composition of the liquid phase at equilibrium (speciation).

3.7 Speciation in the liquid phase

The speciation of the reacting system in the liquid phase as predicted by the VLE model obtained within this article is shown in Figure 5 at a temperature of 40°C and 120°C as a function of the CO_2 loading. These temperatures have been selected since they represent the operating conditions typical of the two most important unit operations in the CO_2 capture process, namely CO_2 absorption and solvent regeneration, respectively. In the absence of experimental data, it is possible only to make some qualitative considerations on the obtained speciation plots and to compare the results with the corresponding speciation provided by Aspen Plus for another primary-tertiary amine blend, namely MEA-MDEA (Figure 6), at the same weight solvent composition (15 wt% primary amine, 40 wt% tertiary amine).

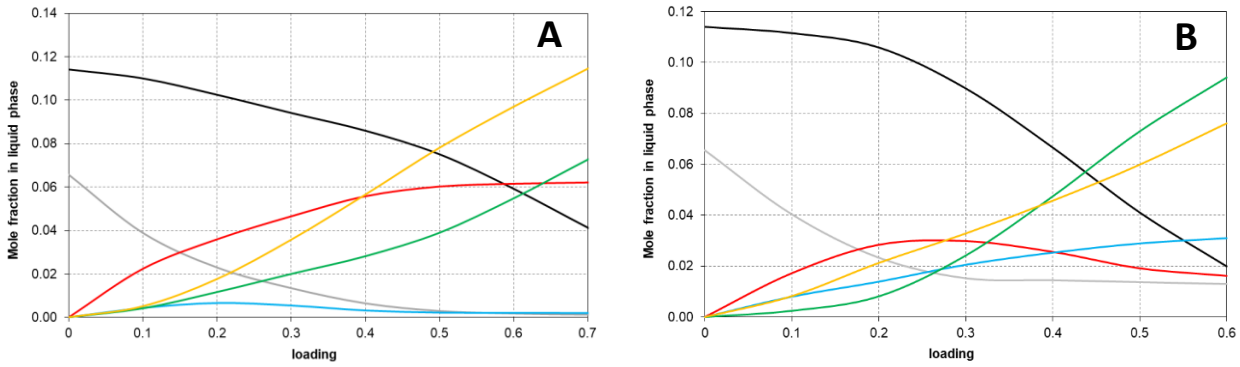


Figure 5. Speciation in the liquid phase predicted by the Aspen Plus ELECNRTL model for HS3 as a function of loading at 40°C (A) and 120°C (B): AP (grey), PRLD (black), APH+ (red), APCOO- (light blue), PRLDH+ (green) and HCO3- (yellow).

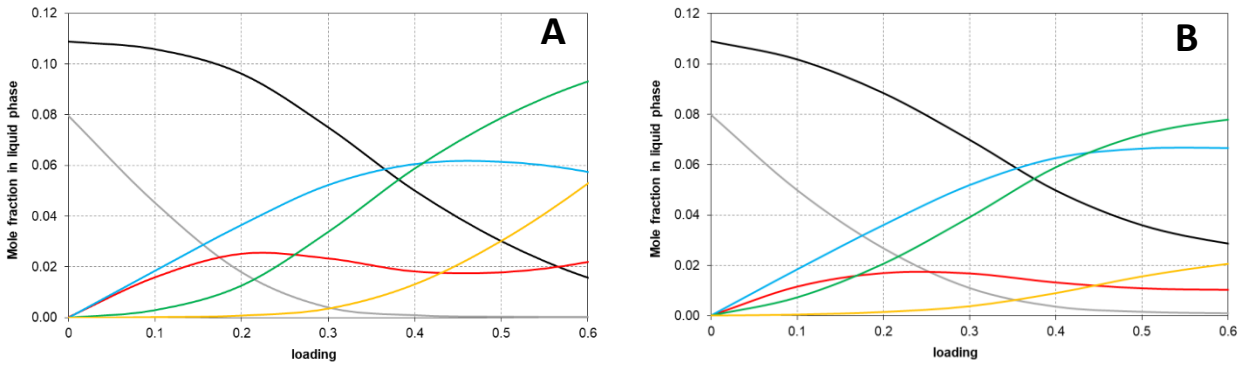


Figure 6. Speciation in the liquid phase predicted by the Aspen Plus ELECNRTL default model as a function of loading at 40°C (A) and 120°C (B) for the MEA-MDEA blend: MEA (grey), MDEA (black), MEAH+ (red), MEACOO- (light blue), MDEAH+ (green) and HCO3- (yellow).

As expected, the primary amine is more reactive than the tertiary amine at low loadings (<0.2), thus it is consumed faster. At higher loadings, PRLD becomes more active than the primary amine, which is associated with an increase in the overall CO_2 absorption capacity of the system. As the tertiary amines reacts, $PRLDH^+$ and HCO_3^- are progressively formed, while the products of AP conversion are APH^+ and $APCOO^-$. Differently from common primary amines such as MEA, which tends to easily form carbamate rather than being protonated, for the HS3 blend amine protonation seems to be favored, thus limiting carbamate formation. In both systems, the carbamate formation reaches a peak at intermediate loadings at low temperature, while it increases until it reaches a steady state value at 120°C. In addition, differently from MDEA, the tertiary amine selected for this blend formulation (PRLD) is very reactive also at high temperature, which is an additional reason for the quite rapid increase in the bicarbonate formation observed both at 40°C and at 120°C. These observations can be justified in light of the outcomes of published experimental work. (Benamor et al., 2015) have demonstrated that AP equilibrium protonation constant is almost 6% higher with respect to the corresponding MEA protonation constant. Moreover, the experimental PRLD protonation constant determined by Liu et al., 2016 is, on average, 5.6 times higher with respect to the MDEA protonation constant, and the discrepancy becomes more pronounced at increasing temperatures, which is a confirmation of the higher reactivity of PRLD with respect to benchmark tertiary amines. As for the reaction heat, a value close to 100 kJ/mole CO_2 which remains constant when the loading lies between 0 and 0.4 is observed for pure AP solution (Bunevska, 2021), while the absorption heat for PRLD is 34 kJ/mol (Liu et al., 2016). In systems where the primary amine is much more reactive than the tertiary one, a quite flat absorption heat profile at low loadings is also observed for the blend (for example in the MEA-MDEA system). In other words, when the carbamate formation dominates over the bicarbonate formation the heat of absorption remains almost constant with the loading, while this is not the case when the most significant contribution is associated with bicarbonate formation. The sudden decrease observed for HS3 absorption heat data at low loadings may thus be motivated by the fact that in this system the bicarbonate formation, in which PRLD plays the key role, becomes competitive even at low loadings, meaning that carbamate formation is not favoured. This behaviour may explain the observed differences in the HS3 speciation plots with respect to the ones associated with the MEA-MDEA reference system.

Heat of absorption

Table 8 gathers the formation enthalpies for AP, PRLD and their corresponding ionic species estimated within this work following the methodology highlighted in section 2.8.1.

By adding those input data to the Aspen model, enthalpy calculations can be performed. Indeed, Aspen Plus calculates the specific enthalpy of a mixture of *n* components (H_{mix}) as the sum of an ideal mixture term, where x_i is the mole fraction and H_i the pure component specific enthalpy, and an enthalpy departure term (H^E_{mix}), whose value is calculated from the activity coefficient (see expression (33).

$$\mathrm{H_{mix}} = \sum_{i=1}^{n} x_i \cdot H_i + H^E_{mix} \qquad (33)$$

The reliability of the energy calculations is checked in Figure 7 by comparing the experimental heat of absorption of CO_2 data for HS3 with the corresponding absorption heat predicted by the model in the whole temperature and CO_2 loading range of interest.

Table 8. Enthalpy of formation of amines, protonated amines and AP carbamate estimated within this work.

Species	ΔH_f^0 [kJ/mol]	Phase
AP	-225.172	Ideal gas
PRLD	-223.147	Ideal gas
APH^+	-313.002	Aqueous
$APCOO^-$	-732.771	Aqueous
$PRLDH^+$	-300.003	Aqueous

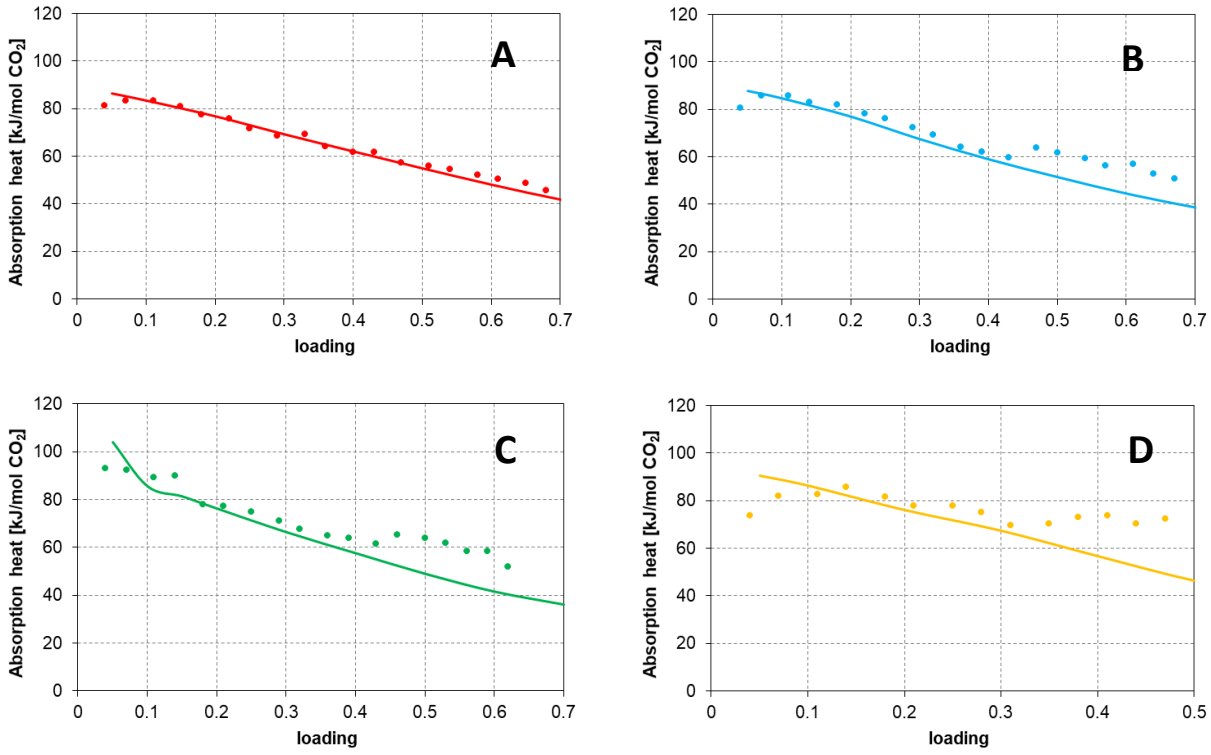


Figure 7. Comparison between the Aspen Plus ELECNRTL model predictions (solid lines) and the experimental data (dots) for the HS3 blend absorption heat at different temperatures: 40°C (A), 60°C (B), 80°C (C) and 100°C (D). Data by Hartono (Hartono et al.).

The model provides a very accurate estimation of the heat of absorption of CO_2 at 40°C (operating conditions of interest for the absorber) in the entire investigated loading range. When the temperature increases, the ELECNRTL model is still accurate in predicting the heat of absorption at low CO_2 loading (0.1 – 0.4), while at

higher loadings an apparent underestimation is observed. However, a trend showing a progressive monotonic reduction of the absorption heat at high loadings, as the one shown by the model, is more realistic and compatible with similar trends observed for other amine systems (Kim et al., 2014, 2009). The only reasonable explanation for an absorption heat trend with a double peak like the one in Figure 7 B) to D) is the presence of a region at intermediate loadings where some precipitation occurs (Kim and Svendsen, 2011). Since precipitation would not be expected in any of the experimental campaigns carried out at NTNU and SINTEF Industry with HS3, the uncommon trend in experimental heat of absorption at high loadings may be associated with experimental inaccuracies, while the trend predicted by the model remains physically meaningful in the whole investigated temperature and loading range.

3.8 Statistics of the regression in Aspen Plus (correlation coefficients analysis)

Finally, we also performed a statistical analysis on the regressed ELECNRTL parameters (GMELCC and GMELCD) to estimate the correlations among these coefficients. The values of the Correlation Coefficients (CoCos) have been directly obtained using the Aspen Plus regression tool. The results are plotted in Figure 8. The CoCos matrix (Figure 8A) enables identifying any potential correlations between the regressed parameters. Linear correlation negatively affects the regression, and it would lead to an overfitting problem which is reflected in stability issues of the ELECNRTL model while solving VLE calculations in flash and absorber/stripper. The CoCos matrix is symmetric and, for this reason, only the left-hand side is reported. The matrix considers all the possible combinations of the ELECNTRL coefficients (both GMELCC and GMELCD) among the 34 coefficients listed in Table 6. All the elements on the diagonal are self-coupled elements, thus by definition, their CoCos are equal to one. However, the elements on the main diagonal are not relevant to the statistical analysis. All the relevant CoCos lie out of the diagonal. When the value of the CoCo approaches the unit, the two parameters are fully linearly dependent, meaning that there is a strong mutual dependence. When CoCo is close to -1, the two coefficients are perfectly anti-correlated, but also in this case there is a strong mutual influence between the two. As a rule of thumb, low values for the CoCos are desired (i.e., close to zero). There is no clear standard indication of which threshold values for the CoCo have been defined to state the correlation between a couple of regressed parameters. The Kirk-Othmer encyclopaedia (Buzzi-Ferraris and Manenti, 2011) just reports some general guidelines (not values), and in the literature, there are no published works suggesting how to handle the CoCo matrix. Further details are reported on websites dedicated to statistical analysis (Andrews.edu, accessed November 2022).

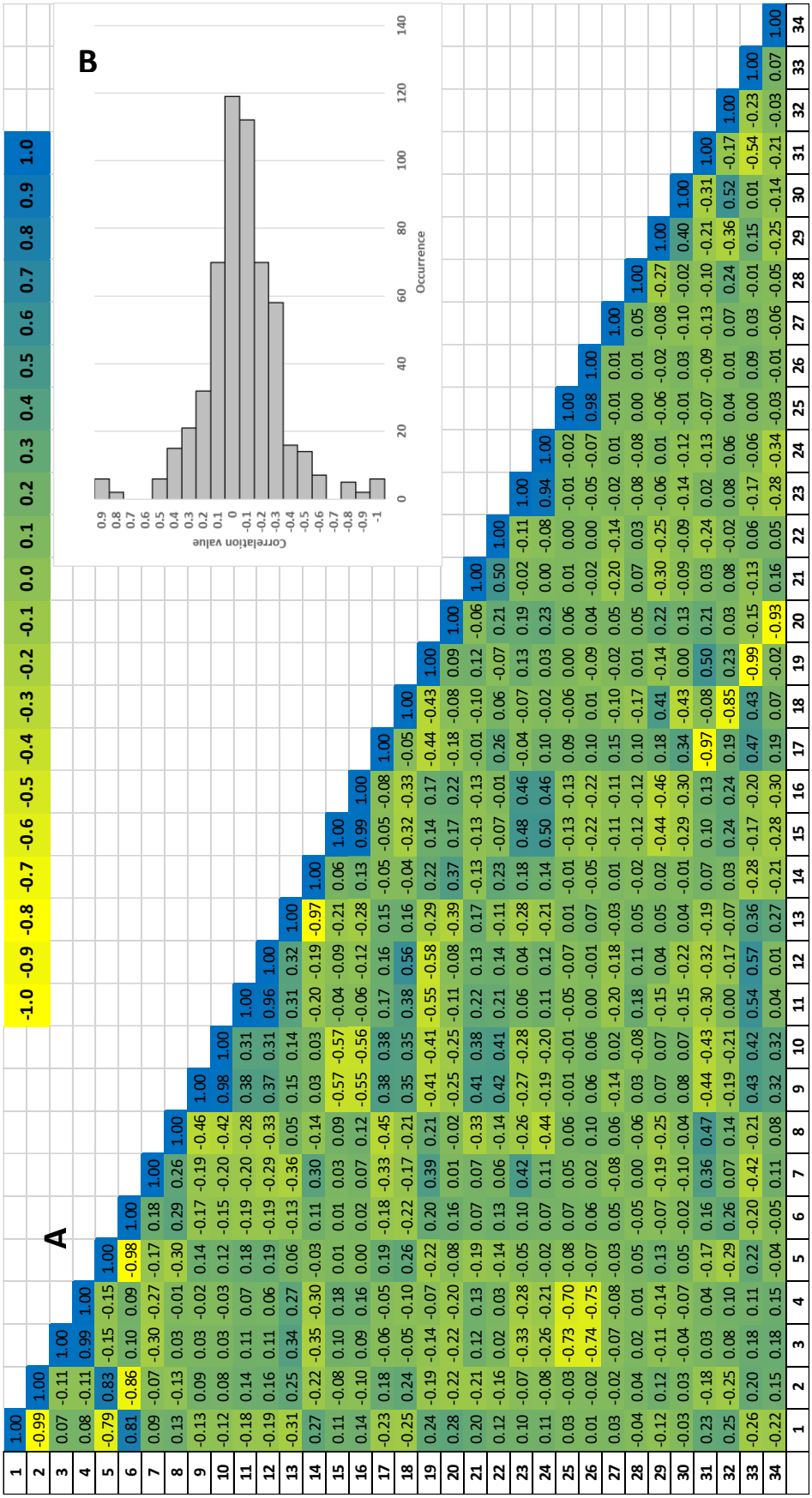
The statistical analysis of the CoCos matrix is reported both in Figure 8B and

Table 9. The results show that the CoCos are normally distributed around the expected null value, and only a few are strongly correlated or anti-correlated. This means that the proposed refit procedure avoids potential correlation issues which may lead to model instabilities. Furtherly, according to the statistical analysis, 94.5% of the coefficients are $|CoCo| < 0.5$, which represents the threshold value to define a weak and almost negligible correlation. In case a more conservative range is considered, 88.8% and 82.2% of the coefficients still lies within the domain $|CoCo| < 0.4$ and $|CoCo| < 0.3$, respectively. These results furtherly confirm the previous comments and point out that correlation does not represent any relevant issue for the proposed model.

689

690 **Table 9 – Results of the statistical analysis on the CoCo**

Range	Occurrence	Frequency
from -1.00 to -0.90	6	1.07%
from -0.90 to -0.80	2	0.36%
from -0.80 to -0.70	5	0.89%
from -0.70 to -0.60	0	0.00%
from -0.60 to -0.50	7	1.25%
from -0.50 to -0.40	14	2.50%
from -0.40 to -0.30	16	2.85%
from -0.30 to -0.20	58	10.34%
from -0.20 to -0.10	70	12.48%
from -0.10 to -0.00	112	19.96%
from 0.00 to 0.10	119	21.21%
from 0.10 to 0.20	70	12.48%
from 0.20 to 0.30	32	5.70%
from 0.30 to 0.40	21	3.74%
from 0.40 to 0.50	15	2.67%
from 0.50 to 0.60	6	1.07%
from 0.60 to 0.70	0	0.00%
from 0.70 to 0.80	0	0.00%
from 0.80 to 0.90	2	0.36%
from 0.90 to 1.00	6	1.07%



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692 **Figure 8. Results of the correlation analysis of the regressed parameters: triangular correlation matrix and relative colour bar scale**
693 **(A) and the distribution of the correlation coefficients (B).**

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4 Conclusions

A detailed general procedure to be followed for the implementation of a new amine-blend model in Aspen Plus® has been presented. Thus, the proposed approach can be applied to any system where the NRTL and ELECNRTL parameters for the activity coefficient should be defined and regressed using experimental data.

Physical CO_2 solubility in an aqueous AP and PRLD blend has been modelled by means of the Henry's constant, which has been fitted to experimental data collected by exploiting the N_2O analogy. The reaction scheme characterizing the primary and tertiary amine interactions with water and CO_2 are defined in compliance with previous models available in Aspen Plus for similar amine blends, while the corresponding equilibrium constants are collected from the literature. ELECNRTL interaction parameters are fitted to in-house VLE data for the HS3 solvent.

The comparison with the experimental data shows that the proposed ELECNRTL model enables predicting VLE with good accuracy. In particular, the new model can predict CO_2 partial pressure with an average relative deviation lower than 18% with respect to all VLE data and lower than 15% if considering the data with partial pressure of CO_2 higher than 1 kPa. The average absolute deviation is limited to 7 kPa. The ELECNRTL model here proposed turns out to be valid under a wide range of temperatures and CO_2 loading, which covers the whole range of operating conditions of interest for both CO_2 absorption and amine regeneration. The proposed model is reliable, providing also insights into the liquid speciation. Furthermore, the Aspen model can be extended to handle both pure amines and their blends since each amine is fully defined as a real component.

The proposed model can predict with high accuracy the absorption heat in the whole investigated temperature (40°C to 100°C) and CO_2 loading (0.03 to 0.7) ranges. This means that the model can be exploited to reasonably estimate the energy requirements and the operating costs of a CO_2 capture plant based on HS3. In addition, the regressed Aspen model provides a reasonable liquid phase speciation which is in line with the observations arising from previous experimental studies carried out with AP and PRLD systems as well as with the HS3 absorption heat in-house data. Finally, a statistical analysis of the correlation coefficients among the interaction parameters demonstrates that no relevant overfitting issues occur, which is important to guarantee the stability of the obtained model.

Dedicated physical property model parameters have been regressed to allow a proper description of the main AP and PRLD properties such as density, viscosity, and specific heat in the liquid phase (see Supplementary Material). Where possible, the fitting procedure is based on both in-house and published data. Interactions between water and amines have also been considered in the regression of water-amine mixtures density and viscosity models. All the property models show appreciable accuracy at all investigated temperatures and compositions.

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