

Process modeling of novel amine carbon capture solvents

Conversion of experimental data into thermophysical and kinetic relations

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MASTER THESIS

for

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Conversion of experimental data for process modeling of novel amine CO₂ capture solvents.

Konvertering av eksperimentelle data for modellering av nye aminbaserte væsker for CO₂ fangst.

Background and objective

Current global electricity generation is heavily dependent on coal which is associated with large emissions of CO_2 . Carbon dioxide capture and storage (CCS) is widely seen as solution to allow use of coal as energy source but with reduced CO_2 emissions. The CO_2 emitted from fuel combustion is captured, transported and sequestered away from the atmosphere.

Among different CO_2 capture technologies, there is an emergence of novel amine solvents for post-combustion capture. These amine solvents hold the promise of lower energy penalty on the coal power plant, of less corrosive behaviour or of other advantageous characteristics when compared to traditional monoethanolamine (MEA) solvents. The novel amines are currently developed and tested in laboratory and pilot environments.

The objective of the master thesis is to make the connection between amine solvent development and implementation of this solvent in a carbon capture process model. The focus is mainly on the implementation of the experimental data into a process modelling tool, using regression tools for thermodynamic and kinetic coefficient estimation. It builds on a previous assignment where a coal power plant with MEA carbon capture was modelled, and novel amines where identified as a possible replacement to MEA. The work would be related to the EDDiCCUT project where different CCS options will be evaluated. A process simulation tool, preferably Apsen Plus, should be used.

The following tasks are to be considered:

- 1. Review of literature related to novel/advanced amine solvents and solvent mixtures.
- 2. Formalize decision criteria and decide on a solvent to be implemented in a process model.
- 3. Investigate which thermophysical/chemical/kinetical relations need to be formulated in order to model the solvent in a process model.
- 4. Regress the coefficients of the relations mentioned under (3) using experimental data from literature or collected from research institutes.
- 5. Validate the regressed relations with respect to experimental results.
- 6. (additionally, and only if time allows, model a simple absorber stripper system with the novel solvent and compare the energy performance of this system to the MEA system modelled in the previous assignment. This explicitly is an extra and is not part of the main master thesis tasks.)

Within 14 days of receiving the written text on the master thesis, the candidate shall submit a research plan for his project to the department/supervisor.

When the thesis is evaluated, emphasis is put on processing of the results, and that they are presented in tabular and/or graphic form in a clear manner, and that they are analyzed carefully.

The thesis should be formulated as a research report with summary both in English and Norwegian, conclusion, literature references, table of contents etc. During the preparation of the text, the candidate should make an effort to produce a well-structured and easily readable report. In order to ease the evaluation of the thesis, it is important that the cross-references are correct. In the making of the report, strong emphasis should be placed on both a thorough discussion of the results and an orderly presentation.

The candidate is requested to initiate and keep close contact with his/her academic supervisor(s) throughout the working period. The candidate must follow the rules and regulations of NTNU as well as passive directions given by the Department of Energy and Process Engineering.

Risk assessment of the candidate's work shall be carried out according to the department's procedures. The risk assessment must be documented and included as part of the final report. Events related to the candidate's work adversely affecting the health, safety or security, must be documented and included as part of the final report. If the documentation on risk assessment represents a large number of pages, the full version is to be submitted electronically to the supervisor and an excerpt is included in the report.

Pursuant to "Regulations concerning the supplementary provisions to the technology study program/Master of Science" at NTNU §20, the Department reserves the permission to utilize all the results and data for teaching and research purposes as well as in future publications.

The final report is to be submitted digitally in DAIM. An executive summary of the thesis including title, student's name, supervisor's name, year, department name, and NTNU's logo and name, shall be submitted to the department as a separate pdf file. Based on an agreement with the supervisor, the final report and other material and documents may be given to the supervisor in digital format.

] Work to be done in lab (Water power lab, Fluids engineering lab, Thermal engineering lab)] Field work

Department of Energy and Process Engineering, 29. January 2014

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Summary

For the development of novel carbon capture solvents, process modeling is a useful tool for (inter alia) the early stage investigation of novel solvents. It represents an option for cheap but detailed prediction of process dynamics and energy requirements without direct investment in pilot plant studies. Thus, it can help to compare different solvent systems and support the decision process for further R&D investments. The number of existing process models for carbon capture solvents is quite scarce compared to the number of promising novel solvents.

This master thesis aims to develop a process modeling procedure for novel post-combustion amine solvents in the process modeling tool Aspen PlusTM. The procedure will promote the development of novel amine solvents and their investigation through carbon capture process models. As a case study, an amine solvent (a piperazine activated aqueous solution of 2-amino-2-methyl-1-propanol) was selected and implemented in Aspen PlusTM. Based on the understanding of the thermodynamic model theory, literature of modeling of carbon capture solvents in Aspen PlusTM and expert elicitation, the data requirement was identified. Moreover, a method for transferring experimental data into the modeling tool to obtain the required correlations was developed and a general modeling procedure was formulated and applied to the selected model. After reviewing and validating of available data from literature and Aspen PlusTM, remaining required parameters were obtained by regression of experimental vapor-liquid equilibrium data and adjustment of parameters. Based on the developed equilibrium model of the solvent system a simple absorption process was modeled, to investigate temperature and concentration profiles over the absorber.

The developed modeling procedure for amine solvents in Aspen PlusTM and the gained experience during the parameter regression facilitates the understanding of the modeling and promotes the use of process simulation tools for the investigation of PCC solvents. However, it also made evident the need for further research and investigation.

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1 Introduction

1.1 Motivation

Increasing recognition about global warming caused by man-made emission of greenhouse gases (GHG) has driven intensive research to reduce CO_2 emissions. As shown in Figure 1-1 around 60% of the CO_2 emissions are caused by the use of fossil fuels. The biggest share, around 40%, of these energy related CO_2 emissions is caused by the combustion of fossil fuels for electricity generation. This shows, that power plants play a central role, when it comes to the reduction of GHG emission.





There are three fundamental paths to achieve a reduction in the emissions caused by electricity generation: the change to less carbon-intensive energy sources like natural gas, nuclear energy and in particular renewable energies; increase in energy efficiency in electricity production and consumption, and the capture and storage of CO_2 from fossil fuel fired power plants. It is predicted by the International Energy Agency (IEA), that nuclear energy and renewable energies can just provide a part of the required power demand for the next decades and that fossil fuels will still remain as a main energy source as shown in Figure 1-2 [3].



Figure 1-2. Predictions for the world electricity generation by fuel until 2040 [3].

The total world coal production has reached a record level of 7831 Mt in 2012 and is increasing by 2.9 % in comparison to previous years [4]. Especially in countries with lacking oil and gas reserves, the ongoing use of coal ensures a certain security of electricity supply in times, where renewable energies cannot deliver due to intermittency of the renewable energy resources. The resulting reduction in emissions due to efficiency increase in coal power plants is limited. The efficiencies of power plants reached a plateau and an increase would demand a further material development effort in case of conventional steam power plants [5]. The carbon capture and storage (CCS) abatement strategy could permit the ongoing use of fossil fuels for electricity generation while reducing the CO_2 emission significantly. However, discussed solutions for the CO_2 storage and utilization have to be further investigated and are not resolved yet.



Figure 1-3: Overview of CO₂ capture processes and systems [6]

CCS refers to the capturing of waste CO_2 from large point sources, such as coal power plants, and its transport to an underground storage reservoir. To separate the CO_2 there are generally three different pathways: post-combustion, pre-combustion and oxyfuel. Figure 1-3 shows the main routes of these three different approaches. A more detailed description can be found in [6]. In this study the focus will be on post-combustion technology, which represents the capturing of CO_2 from flue gases before they are emitted to the atmosphere.

1.1.1 Chemical absorption PCC

There are several CO_2 separation technologies for post-combustion capture (PCC) in coal-fired power plants including adsorption, cryogenics, membranes and absorption. CO_2 recovery using chemical absorbents is one of the most and in great width studied technology of these options [7]. Figure 1-4 shows a simplified concept for a chemical absorption-desorption process for CO_2 capture in a coal-fired power

plant. The flue gas is fed into the absorber where the CO_2 is absorbed into a chemical solvent, while the treated flue gas is released to the atmosphere. The CO_2 rich solvent is then fed to a desorption column (stripper) for regeneration and the captured CO_2 is transported to a compression unit. In a power plant, the required heat for solvent regeneration is covered by a steam supply from the power plant.



Figure 1-4: Simplified process flow diagram of a chemical absorption-desorption process for CO₂ capture with MEA [8]

As mentioned before, amine scrubbing for CO_2 capture from gas streams is not a new one. Already in 1930 Bottoms patented the basic process of CO_2 absorption from fuel gas or combustion gas into an aqueous amine solution [7]. Since 1978 several commercial plants for CO_2 capture have been commissioned worldwide (see Table 1-1). Although there is an extended list of commercially operated CO_2 capture units, these plants have been applied to industrial CO_2 containing feed streams.

The commercial large scale application to power plants still faces obstacles such as high energy requirements, cost and solvent losses, which makes it not feasible yet. The biggest part of the energy requirement for post-combustion CO_2 capture is demanded by solvent regeneration in the stripper. But also solvent degradation, corrosion, solvent volatility and environmental impact of the solvent are drawbacks, which need to be overcome [9-12].

Company	Capacity	Solvent	Commissionin g	Reference
Kerr-	800 tons/day		1978	
McGee/ABB	200 tons/day	20 wt-% MEA	1991	[13, 14]
Lummus	300 tons/day		1991	
Dow Chemical/Union Carbide	1200 tons/day	30 wt-% MEA	1982	[15]
	several appl.	Econamine FG	1020	
Fluor Daniel Inc.	up to 320	Econamine FG	2003	[16, 17]
	tons/day	Plus	Plus 2005	
	> 10 appl.	KS-1	1999	
KEPCO/MHI	up to 450	KS-2	-	[18, 19]
	tons/day	KS-3	2012	
Test Centre				
Mongstad	100,000	Amine/ chilled	2012	[20, 21]
(Aker Clean	tons/year	ammonia	2012	[20, 21]
Carbon/Alstom)				
Casolv Techn.	na	DC-101, DC-103,	na	[22 23]
Inc.	11.a.	DC-103B	11.a.	[22, 23]
HTC Purenergy	4 tons/day	PSR	-	[24]

Table 1-1: Amine based commercial processes form 1978

1.1.2 R&D of novel solvents for PCC

The targeted research and development of novel solvents with specific characteristics can help to reduce the resulting efficiency penalty and costs and make the commercialization of post combustion capture feasible.

Common solvents used for CO_2 absorption are simple primary, secondary and tertiary amines as well as sterically hindered amines. But also amino acid salt solutions are under investigation for their use in PCC. These different types of solvents exhibit different properties related to key properties for CO_2 capture such as absorption capacity, reaction kinetics, degradation tendency and regeneration potential and facility as well as toxicity and biodegradability.

1.1.3 Process modeling of novel solvents for PCC

Before novel solvents are tested in a pilot plant scale detailed laboratory experiments are performed to point out potential promising novel solvents based on their CO₂ absorption rate, CO₂ loading capacity and heat of reaction. For the further investigation, process modeling is a widely used tool to simulate the capture process and determine the process energy requirements and costs. Process modeling represents an option for cheap but detailed prediction of process dynamics and energy requirements without the direct investment in complex pilot plant studies. Thus, it can help to compare different solvent systems and support the decision process for further R&D investments. A preferred process simulation tool for the purpose of modeling chemical solvents for CO₂ capture is Aspen PlusTM, due to detailed databases and good physical property methods. Another advantage is an integrated regression tool, which allows user defined regression of experimental data into thermophysical and kinetic parameters for specific solvent systems, whose parameters are not available in the databases. For a number of single amine-based solvent systems as well as some blended amine-based systems the thermophysical and kinetic parameters from regressed experimental data is available in the Aspen Plus databanks or Aspen Plus examples (see Table 1-2).

Table 1-2: Available amine-based solvent systems in Aspen [25]

Single solvent system	Blended solvent systems
AMP, DEA, DGA,	MEA/MDEA,
DIPA, MDEA, MEA,	MDEA/PZ, MEA/PZ,
NH3, PZ, TEA	Sulfolane/DIPA,
	Sulfolane/MDEA

However, the number of process models of novel solvents, especially of blended solvents, is quite small compared to the advantage they provide for the R&D of novel better performing solvents. A couple of reports on the implementation of novel solvents into Aspen Plus have been published. Dash et al. presented the results of a simulation study using an aqueous blend of AMP/PZ [26]. Within this study, the thermodynamic and kinetic parameters have been obtained by the regression of experimental data from previous experimental investigations and literature [27-32]. A second example is the modeling of an amino acid salt system reported by Aronu et al.,

[33], where the model parameters have been estimated based on vapor-liquid equilibrium (VLE) measurements and total pressure measurements. The comparison of the list of available solvent models (see Table 1-2) and the list of the investigated solvents for CO_2 capture shows clearly that there is a need for further implementation of novel solvent systems in process modeling tools.

1.2 Research goal and related research questions

The research goal of this master thesis is to develop a process modeling procedure for novel post-combustion amine solvents in order to promote the development of novel amine solvents and their investigation through carbon capture process models. For this, a novel solvent is selected and implemented in the process modeling tool Aspen PlusTM. It includes the implementation of experimental data into the process modeling tool to obtain the required thermophysical, chemical and kinetic relations of the thermodynamic model.

From the research goal the following research questions are derived:

- Which novel post-combustion carbon capture solvent is suitable as case study for the implementation in Aspen PlusTM?
- What are the data requirements for the thermodynamic modeling of PCC solvents?
- How can experimental data be included in the modeling tool to obtain the required correlations/parameters?

2 Methodological approach

In the following section the methodological approach is summarized.

For the selection of a novel post-combustion carbon capture solvent to be implemented in Aspen PlusTM, the first step is to make an inventory of novel post-combustion carbon capture solvents based on a detailed literature research. In order to assess and select a solvent, criteria have to be developed related to the requirements for thermodynamic modeling of solvents in Aspen PlusTM.

The requirements for the thermodynamic modeling are ascertained based on the theory of the applied thermodynamic model in (see Chapter 4). The comprehension of the theory behind the thermodynamic model, on the one hand, allows understanding the data requirements and, on the other hand, point out interactions among the thermodynamic relations, which helps to understand the influence of given parameters on the model behavior.

Based on the understanding of the model theory, publications about modeling of carbon capture solvents in Aspen PlusTM and expert elicitation, a method to transfer experimental data into the modeling tool to obtain the required correlations is developed and a general modeling procedure is formulated.

In a next step, the developed procedure is applied to the selected solvent. This includes reviewing available data, validating

those and regressing missing data to obtain the thermodynamic model. In the last step, the obtained thermodynamic model is validated based on selected properties relevant for post-combustion CO_2 capture.

The complete methodological approach applied in this work, is summarized and visualized in the flowsheet in Figure 2-1.



Figure 2-1. Flowsheet of the applied methodological approach.

3 Solvent selection

3.1 Selection criteria

The following properties represent the characteristics of an ideal solvent for PCC CO_2 capture [34].

- High inherent CO₂ capacity per weight of solvent
- High absorption rate
- Low cost
- Non-corrosive behavior
- No degradation under the operating conditions of the absorber and desorber
- Low vapor pressure
- Low viscosity
- Non-toxic and non-hazardous

Besides the assessment of the properties there is another very important criterion for solvent selection. To ensure the feasibility of the thermodynamic modeling one of the most important criterion is data availability. Not only for the pure components, but also for the ionic and molecular solute species, scalar and temperature dependent physical properties are required. The exact type of physical properties required for these types of species are reviewed in Table 3-1 and discussed in more detail in Chapter 4.1.1 and 4.1.2. This physical property data requirement is however not an exclusionary criterion. In case that these properties are not available in Aspen PlusTM and also cannot be provided by experimental data, the estimation tool within Aspen PlusTM can be used to estimate some of the missing parameters. This tool predicts pure organic component properties based on several different molecule group-contribution methods. Within these methods, the molecule structure is divided into groups. Based on their quantity and functionality the missing properties are estimated. For more information on property estimation methods can be found in [35]. A list of the physical properties, which can be determined with these estimation methods, and the applicable methods for the specific properties can be reviewed in Appendix A in Table A - 1.

MOLECULES			IONS
Parameter	Explanation	Parameter	Explanation
DGFORM	Standard free energy of	CHARGE	Ionic Charge number
	formation for ideal gas at		(positive for cations,
	25 deg C		negative for anions)
DHFORM	Standard enthalpy of	DGAQFM	Aqueous phase free energy
	formation for ideal gas at		of formation at infinite
	25 deg C		dilution and 25 deg C. For
			ionic species and
			molecular solutes in
			electrolyte systems
DHVLB	Enthalpy of vaporization at	DHAQFM	Aqueous phase heat of
	ТВ		formation at infinite
			dilution and 25 deg C. For
			ionic species and
			molecular splutes in
			electrolyte systems
MW	Molecular weight	MW	Molecular weight
OMEGA	Pitzer acentric factor	RADIUS	Born radius of ionic
PC	Critical pressure	ZWITTER	species Identifies zwitterions; Set
			the parameter to 1 for a
			zwitterion and 0 for other
			components.
RKTZRA	Parameter for the Rackett		
	liquid molar volume model		
ТВ	Normal boiling point		
TC	Critical temperature		
VC	Critical volume		

Tuble e 11 Required Section properties for molecules and tons

ZC	Critical	compressibility	
	factor		

Table 3-2. Required T-dependent physical properties for molecules and ions.

MOLECULES		I	ONS
Parameter	Explanation	Parameter	Explanation
CPDIEC	Pure component	CPAQ0	Aqueous phase heat
	dielectric constant		capacity at infinite
	coefficients of		dilution polynomial
	nonaqueous		
	solvents		
CPIG or	Ideal gas heat	PLXANT	Coefficients for the
CPIGDP	capacity		Extended Antoine
			vapor pressure
			equation for a
			liquid
DHVLWT or	Vaporization	VLBROC	Brelvi-O-Connell
DHVLDP	equation for pure		Volume Parameter
	components		
PLXANT	Coefficients for the		
	Extended Antoine		
	vapor pressure		
	equation for a		
	liquid		
VLBROC	Brelvi-O-Connell Volume Parameter		

3.2 Solvents for post-combustion CO₂ capture

Common solvents used for CO_2 absorption are simple alkanolamines and sterically hindered amines. Amines are organic derivatives of ammonia, in which one or more of the hydrogen atoms are replaced by an organyl group. Depending on the number of the replacements they can be classified into primary, secondary and tertiary amines. Sterically hindered amines represent either a primary amine in which the amino group is attached to a tertiary carbon, or a secondary amine in which the amino group is attached to at least one secondary or tertiary carbon [36]. These different types of alkanolamines exhibit different advantageous and disadvantageous properties related to the key properties for CO_2 capture - absorption capacity, reaction kinetics, degradation tendency and regeneration potential and facility as well as toxicity and biodegradability.

Table 3-3: Summarized	solvent properties	of alkanolamines,	ammonia	and a	alkali	salts
[34]						

	heat of	absorption	CO ₂	degradation
	absorption	rate	capacity	tendency
primary	•	•	0	•
amines	-	-	-	-
secondary		0	0	•
amines	-	-	-	-
tertiary	0	0	•	0
amines	-	-	-	-
steriacally		0		0
hindered amines	•	, and the second s	•	Ũ
polyamines	•	•	\bullet	0
alkali salts	0	0	●	0
ammonia	0	0	●	0

• high, • medium, \circ low

The key advantage of primary and secondary alkanolamines is their fast reactivity due to the formation of stable carbamates. However this leads to a high solvent regeneration energy requirement. Another drawback is the relatively low CO_2 absorption capacity, which is limited to 0.5 mol CO_2 per mol amine [37]. Tertiary alkanolamines have a low reactivity with respect to CO_2 , due to the exclusive formation of bicarbonates by CO_2 hydrolysis. However, this leads to a very low solvent regeneration energy requirement. An advantage is the high CO_2 loading capacity of theoretically 1 mol CO_2 per mol amine [X]. The application of sterically hindered amines can offer absorption capacity, absorption rate, selectivity, and degradation resistance advantages over conventional amines for CO_2 removal. The use of blended alkanolamines allows combining advantages of amines, for example, the fast reactivity of primary and secondary amines and the high CO_2 loading capacity and low solvent regeneration energy requirement of tertiary and sterically hindered amines.

An interesting alternative for alkanolamines is the use of aqueous alkaline salts of amino acids. Generally, amino acid salt solutions can be characterized by lower vapor pressures due to their ionic nature, higher stability towards oxidative degradation and a chemical reactivity with CO_2 comparable or even higher than those of alkanolamines. Besides this they have the advantage of a low environmental impact and a high biodegradability [38, 39]. A further interesting feature is their ability to precipitate solids when absorbing CO_2 . This can reduce the effort for the separation of the CO_2 , but also requires the development of a new process concept [40] [41]. The pros and cons of the properties of alkanolamines, ammonia and alkali salts are summarized in Table 3-3 [34].

Several novel solvents are discussed and investigated for the application in the field of post-combustion CO_2 capture. An extended list of well-studied as well as novel solvents is shown in Appendix A in Table A - 2. The data availability is classified into low, medium and high based on the literature review. Although the single solvents have not been studied in detail due to the high quantity of solvents, the extended literature review gives a good overview. The list of potential blends of amines is expected to be unlimited due to the endless variation of the different amines. In Appendix A in Table A - 3 some examples for investigated amine blends are summarized.

3.3 Selection

As shown in Table A - 2, the list of amines for post combustion CO_2 capture is long. Still for most amines data availability is very low. Based on this comparison, two solvent systems have been selected for further screening of their ability to be modeled within this research work – an aqueous solution of the amino acid salt potassium taurate (KTAU) and a piperazine (PZ) activated aqueous solution of 2-amino-2methyl-1-propanol (AMP).

3.3.1 Aqueous solution of potassium taurate

Potassium taurate is the potassium salt of the amino acid taurine. As described earlier amino acid salts (AAS) have certain advantages over conventional amines, e.g. lower toxicity, higher biodegradability, negligible volatility and, for some, a high resistance to oxidative degradation [38, 39]. Due to this, the interest in the performance of AAS has grown and their absorption characteristics are under extensive research. Different process concepts have been investigated for the application of amino acid salts for post-combustion CO_2 capture. Recently a process configuration called DECAB Plus process has been investigated by TNO to handle solids and use the precipitating ability of amino acid salts. A detailed description of this process can be seen in [42]. To analyze and compare this new concept to the conventional MEA case key properties (such as specific reboiler duty, absorption enthalpy, separator energy and pH, of the absorption and desorption in precipitating amino acid salts) have been investigated based on an aqueous solution of potassium taurate. Within [42] a process model has been developed to evaluate the process.



Figure 3-1. Molecule structure of taurine

The aqueous potassium taurate system is chosen for a further screening due to the quite high data availability related to the described study and an offer by TNO to eventually conduct more experiments to determine missing component physical properties in their laboratories. During the screening process the availability of the required physical property parameters for the participating components (KOH, taurine, taurine ions) has been checked in the databases from Aspen PlusTM. The outcome of this screening showed, that there are just a few physical properties available for taurine in the Aspen PlusTM databases and in the data sources NIST and DECHEMA as can be seen in Table 3-4. For the taurine ions no physical properties could be found in the databases and literature and it is also not possible to estimate physical properties for joure organic compounds. Thus, the minimum required information for the ions, the aqueous phase free energy of formation (DHAQFM) and the aqueous phase heat capacity at infinite dilution (CPAQ0), is missing.

Table 3-4. Available parameters for taurine in the Aspen PlusTM, NIST and DECHEMA databases.

Unit	Taurine	Source
J/kmol	-774605000	DB NIST-TRC
-	125.149	DB NIST-TRC
-	0.249941	DB LEBAS
K	759 K	DB NIST-TRC
	Unit J/kmol - - K	UnitTaurineJ/kmol-774605000-125.149-0.249941K759 K

Due to the low data availability compared to required data (Table 3-1 and Table 3-2), an attempt is made to estimate the physical properties of taurine based on the in Aspen PlusTM implemented group-contribution methods as described in Chapter 3.1. For this the taurine molecule structure (see Figure 3-1) has to be described by its groups, which differ for each group-contribution method. In most cases the exact required groups, that describe the taurine molecule, were not available. However, for one group
contribution method, called JOBACK, it was possible to describe the molecule structure (see Table 3-5) and parameters could be estimated. The results of the scalar parameter estimation are summarized in Table 3-5. The estimation results of the temperature dependent parameters can be reviewed in Appendix A in Table A - 4.

 Table 3-5. Selected groups from JOBACK method for the parameter estimation of taurine.

		Number of
Group number	Group	occurrence
101	-CH ₂ -	2
119	-OH	1
128	=0	2
129	-NH ₂	1
139	-S-	1

 Table 3-6. Estimated scalar parameters for taurine.

Parameter	Unit	Value	Method
ТВ	K	457.65	JOBACK
TC	Κ	632.731	JOBACK
PC	kPa	8175	JOBACK
VC	cum/kmol	0.3215	JOBACK
DHFORM	kJ/kmol	-656400	JOBACK
DGFORM	kJ/kmol	-572950	JOBACK
OMECA	-	0 221507	DEFINITION
OMEGA		0.221397	(TC, PC, PL)
	1r I/Irm o1	42020 1	DEFINITION
DHVLD	KJ/KIIIOI	42929.1	(TC, PC, PL)
70		0 416497	DEFINITION
ZC	-	0.410487	(TC, PC, VC)
		I I	

ργττρα		0 27076	GUNN-YAMADA
KKIZKA	-	0.27070	(TC, PC OMEGA)

The comparison of the estimation results with the available parameters is presented in Table 3-7. Just the critical temperature TC and the parameter for the Rackett liquid molar volume model RKTZRA can be compared, as no other data is available for the estimated values, either in the database, nor in literature. The estimated values deviate from the available parameters, RKTZRA about 8% and the TC about 17%. Due to this estimation results it can be assumed, that also the other estimated parameters deviate from the real behavior of taurine.

 Table 3-7. Comparison of estimation results with available parameters from the database.

Parameter	Unit	Estimated	Database	Deviation
RKTZRA	-	0.27076	0.249941	8 %
TC	K	632.731	759	-16.6 %

The comparison of the database values and estimated values leads to the conclusion, that the estimation results for taurine are not sufficient enough to be used for the development of a thermodynamic model. For the development of a thermodynamic model in Aspen PlusTM, as a first step, there is a need for further experimental investigation of the physical properties of the participating components.

3.3.2 PZ activated aqueous solution of AMP

The PZ activated aqueous solution of AMP, hereafter called PZ/AMP solvent system, is also known as CESAR 1 solvent and has already been investigated in a pilot plant study in the EU project CESAR (CO₂ enhanced Separation and Recovery)[43]. Within this research project the PZ/AMP solvent system has been modeled in the simulation tool CO₂SIM, a flowsheet simulator for CO₂ absorption processes [44].

Unrelated to this project, this solvent also has been modeled in Aspen PlusTM in one publication series by the Indian Institute of Technology Kharagpur. These publication series contains a presentation of vapor-liquid equilibrium thermodynamic models for the two sub-component systems PZ-H₂O-CO₂, AMP-H₂O-CO₂ and the quaternary system PZ-AMP-H₂O-CO₂ [29-31]. Within this works the required interaction parameters for the used thermodynamic model (elecNRTL, see Chapter 4) have been regressed with experimental VLE data for different concentrations and temperatures. For the quaternary system data on the rate of absorption of CO₂ into PZ activated concentrated aqueous solutions of AMP is reported [28]. Finally, based on the thermodynamic and kinetic parameters from the previous work and literature an absorption-regeneration process has been modeled in Aspen PlusTM using a RadFrac-RateSep block .

The required physical properties for the molecule species PZ and AMP and the ionic species AMPH⁺, PZH⁺, PZCOO⁻, PZ(COO⁻)₂ and H⁺PZCOO⁻, which are occurring in the liquid phase of the solvent, are already implemented in the Aspen Plus database or available in Aspen examples. These properties are reviewed in Chapter 4.1.

3.3.3 Final selection

After further screening of the potassium taurate solvent system and the PZ/AMP solvent system a final selection of the solvent system to be modeled was made. In Chapter 3.3.1 is shown, that the available data for the potassium taurate system does not comply with the data requirement for the thermodynamic modeling in Aspen PlusTM. The estimation results of the physical properties of the molecule species taurine do not have sufficient accuracy and the physical properties for the ionic species cannot be estimated with the in Aspen PlusTM implemented group estimation methods. Thus, for this system, a first step towards the thermodynamic modeling in Aspen PlusTM would be a further experimental investigation of the participating species to determine the required physical properties. This research cannot be done within the time scope of this work and also not match with the research objective of this work, which focuses rather on the data regression procedure in Aspen PlusTM.

As described in Chapter 2.3.2, for the PZ/AMP solvent system the required physical properties are implemented in the Aspen PlusTM database or available in Aspen PlusTM examples. Besides this experimental VLE data is available, which allows the regression of parameters to describe a thermodynamic equilibrium model. Additionally, modeling results from the AMP-PZ system has been published, which would allow the validation of this work.

The conculsions of the further screening lead to the decision to model the PZ/AMP solvent system in Aspen PlusTM.

4 Electrolyte NRTL thermodynamic model

Aqueous solutions of amines represent electrolyte systems, which means that the amine molecules ionize when they are dissolved in water. In electrolyte solutions a larger variety of interactions and phenomena exist than in non-electrolyte solutions. Besides physical and chemical molecule-molecule interactions, ionic reactions and interactions occur (molecule-ion and ion-ion). For the thermodynamic modeling of this kind of systems the electrolyte nonrandom two-liquid model (elecNRTL) is applied [45]. This chapter serves to describe the models and equations, which are used within the elecNRTL model. Table 4-1 summarizes the models and equations used for the calculation of the physical properties in the liquid and vapor phase and shows the interaction dependencies among the models. These models for the liquid and vapor phase properties are explained in more detail in the following two sections. After the model description the data requirement for the application of elecNRTL is summarized.

Thermodynamic property	models/ equations						
FF)							
	Liquid Phase						
Enthalpy	Electrolyte NRTL enthalpy model						
	Required sub-models:						
	• General pure component ideal gas heat capacity						
	• General pure component heat of vaporization						
	• Electrolyte NRTL activity coefficient model						
	Aqueous Infinite Dilution Heat Capacity						
Gibbs energy	Electrolyte NRTL Gibbs free energy model						
	Required sub-models:						
	• General pure component ideal gas heat capacity						
	• Electrolyte NRTL activity coefficient model						

Table 4-1. Applied thermodynamic models and equations within the elecNRTL model.

	Aqueous Infinite Dilution Heat Capacity
Entropy	Relation between Gibbs free energy, Enthalpy and Entropy ¹
	• Electrolyte NRTL enthalpy model
	• Electrolyte NRTL Gibbs free energy model
Density	Clarke aqueous electrolyte volume
	Required sub-model:
	• Rackett equation
Activity coefficients	Electrolyte NRTL activity coefficient model
Fugacity ²	Brelvi-O'Connell model
	Electrolyte activity coefficient model
	Extended Antoine
	Henry's law
	Rackett equation
	Soave-Redlich-Kwong
	Vapor phase
Enthalpy,	Soave-Redlich-Kwong
Gibbs energy,	General pure component ideal gas heat capacity correlation
Entropy	
Fugacity coefficient	Soave-Redlich-Kwong
Density	

4.1 Liquid phase

In this section the models used for the thermodynamic description of the liquid phase physical properties are presented. For each model the data requirement is summarized. The physical properties, which are constantly used in the Aspen PlusTM models presented in this work and that do not vary for the different models, are presented in this chapter. The physical properties, for which different values are used in the presented models, are presented later in this work.

¹ The Gibbs free energy is an thermodynamic quantity combining enthalpy and entropy; G = H - TS

² Calculation of liquid phase fugacity is described in Chapter 4.3 Vapor-liquid equilibrium calculations.

4.1.1 Electrolyte NRTL enthalpy model

Using the electrolyte NRTL enthalpy model the liquid phase molar enthalpy H_m^* is calculated as follows:

$$H_m^*(T) = x_w H_w^* + \sum_s x_s H_s^{*,l} + \sum_k x_k H_k^\infty + H_m^{*E}$$
4-1

Where

 x_w , x_s , x_k are the mole fraction of water (w), non-water solvent (s) and ion or molecular solute (k),

 H_m^{*E} is the liquid phase excess molar enthalpy,

 $H_w^*(T)$ is the liquid enthalpy for water,

$$H_{w}^{*}(T) = \Delta_{f} H_{w}^{*,ig}(T^{ref}) + \int_{T^{ref}}^{T} C_{p,k}^{ig} dT$$
4-2

Where,

 $\Delta_f H_w^{*,ig}$ is the Standard enthalpy of formation for ideal gas at 25 °C, $C_{p,k}^{ig}$ is the ideal gas heat capacity

 $H_s^{*,l}(T)$ is the liquid enthalpy for non-water solvents,

$$H_{s}^{*,l}(T) = H_{s}^{*,lg}(T) - \Delta H_{s,vap}(T)$$
4-3

Where,

 $H_s^{*,ig}$ is the ideal gas enthalpy of non-water solvents, and, $\Delta H_{s,vap}$ is the enthalpy of vaporization of non-water solvents.

and, $H_k^{\infty}(T)$ is the aqueous infinite dilution enthalpy:

$$H_k^{\infty}(T) = \Delta_f H_k^{\infty,aq}(T^{ref}) + \int_{T^{ref}}^T C_{p,k}^{\infty,aq} dT$$

$$4-4$$

Where, $\Delta_f H_k^{\infty,aq}$ is the aqueous phase heat of formation at infinite dilution and 25 °C for ionic species and molecular solutes, and, $C_{p,k}^{\infty,aq}$ is the aqueous infinite dilution heat capacity.

For this calculations $C_{p,k}^{ig}$ is obtained from the ideal gas heat capacity model (see Chapter 4.1.4), $\Delta H_{s,vap}$ from the heat of vaporization model (see Chapter 4.1.5) and $C_{p,k}^{\infty,aq}$ from the aqueous infinite dilution heat capacity model (see Chapter 4.1.6). H_m^{*E} is calculated based on the electrolyte NRTL activity coefficient model (see Chapter 4.1.3) with the following equation:

$$H_m^{*E} = -RT^2 \sum_i x_i \frac{\delta \ln \gamma_i}{\delta T}$$

$$4-5$$

The parameter requirements for this model and the values used for the components AMP, PZ, H_2O and CO_2 are summarized in Table 4-2.

Table 4-2. Parameter requirements for the electrolyte NRTL enthalpy model.

Physical	Parameter	Unit		Com	onents	
property	in Aspen	Unit		Com	Jonents	
			AMP	PZ	H ₂ O	CO_2
$\Delta_f H_w^{*,ig}$	DHFORM	kJ/mol	-270290^{1}	16400^2	-241997 ³	-394647.8 ³
			$AMPH^+$	PZH^+	PZCOO ⁻	$PZ(COO^{-})^{2}$
$\Delta_f H_k^{\infty,aq}$	DHAQFM	kJ/mol	-368000^{1}	-110550 ¹	-498695.2^{1}	-971930 ¹
			H ⁺ PZCOO ⁻	HCO ₃ ⁻	CO_{3}^{-2}	OH
$\Delta_f H_k^{\infty,aq}$	DHAQFM	kJ/mol	-589500.6 ¹	-691990 ¹	-677140^{1}	-229994^{1}
			$H^{3}O^{+}$			
$\Delta_f H_k^{\infty,aq}$	DHAQFM	kJ/mol	-285830^{1}			
Source (Aps	sen Plus TM Dat	abases): 1	DB-AOUEOU	S^{2} DB-PUR	E28. ³ DB-ASE	PENCD

4.1.2 Electrolyte NRTL Gibbs free energy model

The equation of the electrolyte NRTL Gibbs free energy model is:

$$G_m^* = x_w \mu_w^* + \sum_s x_s \mu_s^{*,l} + \sum_k x_k \mu_k^\infty + RT \sum_j x_j \ln x_j + G_m^{*E}$$
4-6

Where,

 x_w , x_s , x_k are the mole fraction of water (w), non-water solvent (s) and ion or molecular solute (k),

 μ_w^* is the molar Gibbs free energy of pure water,

 $\mu_s^{*,l}$ is the Gibbs free energy of a non-water solvent,

 μ_k^{∞} is the aqueous infinite dilution thermodynamic potential,

 $RT \sum_{i} x_{i} \ln x_{i}$ is the ideal mixing term, where j refers to any component,

R is the ideal gas constant,

T is the temperature, and,

 G_m^{*E} is the molar excess Gibbs free energy.

The molar excess Gibbs free energy G_m^{*E} is calculated based on the electrolyte NRTL activity coefficient model (see Chapter 4.1.3) with the following equation:

$$G_m^{*E} = RT \sum_i x_i \ln \gamma_i \tag{4-7}$$

The thermodynamic potential μ_k^{∞} is calculated based the infinite dilution aqueous phase heat capacity polynomial as followed:

$$\mu_k^{\infty} = G_k^{\infty} = H_k^{\infty} - TS_k^{\infty} + RT \ln\left(\frac{1000}{M_w}\right)$$

$$4-8$$

$$H_k^{\infty}(T) = \Delta_f H_k^{\infty,aq}(T^{ref}) + \int_{T^{ref}}^T C_{p,k}^{\infty,aq} dT$$

$$4-9$$

$$S_k^{\infty} = \frac{\Delta_f H_k^{\infty,aq} - \Delta_f G_k^{\infty,aq}}{T^{ref}} + \int_{T^{ref}}^T \frac{C_{p,k}^{\infty,aq}}{T} dT$$

$$4-10$$

Where,

 M_w is the molecular mass of water,

 $\Delta_f H_k^{\infty,aq}$ is the infinite dilution aqueous phase enthalpy of formation for component k, $C_{p,k}^{\infty,aq}$ is the aqueous infinite dilution heat capacity for component k, and,

 $\Delta_f G_k^{\infty,aq}$ is the infinite dilution aqueous phase standard Gibbs free energy for component k.

For the calculations $C_{p,k}^{\infty,aq}$ is obtained from the aqueous infinite dilution enthalpy model, and $\Delta_f H_k^{\infty,aq}$ from the input requirements of the electrolyte NRTL enthalpy model.

The data requirements for this model and the used values for each component are summarized in Table 4-3.

Physical	Parameter	Unit		Comp	oonents	
property	III Aspell					
			AMP	PZ	H ₂ O	CO_2
$\Delta_f G_w$	DGFORM	kJ/mol	-84730 ¹	170000 ²	-228572^{3}	-394370 ³
			$AMPH^+$	PZH^+	PZCOO ⁻	$PZ(COO^{-})^{2}$
$\Delta_f G_k^{\infty,aq}$	DGAQFM	kJ/mol	-162805.4^4	90948 ¹	-213380 ¹	-566680 ¹
			H ⁺ PZCOO ⁻	HCO ₃ ⁻	CO_{3}^{-2}	OH
$\Delta_f G_k^{\infty,aq}$	DGAQFM	kJ/mol	-267580^{1}	-586770 ¹	-527810 ¹	-157244 ¹

Table 4-3. Parameter requirements for the electrolyte NRTL Gibbs free energy model.

			$H^{3}O^{+}$		
$\Delta_f G_k^{\infty,aq}$	DGAQFM	kJ/mol	-237129 ¹		
~				2	

Source (Apsen PlusTM Databases): ¹ DB-AQUEOUS, ² DB-PURE28, ³ DB-ASPENCD, ⁴ Aspen PlusTM example

4.1.3 Electrolyte NRTL activity coefficient model

An activity coefficient model accommodates non-ideality into a thermodynamic model. When it is applied to vapor-liquid equilibrium calculations, the activity coefficients can only be used for the liquid phase. For the vapor phase usually an equation of state is used (see Chapter 4.2). The molar Gibbs free energy within the elecNRTL model is described by the following equation (see Chapter 4.1.2):

$$G_m^* = x_w \mu_w^* + \sum_s x_s \mu_s^{*,l} + \sum_k x_k \mu_k^\infty + RT \sum_j x_j \ln x_j + G_m^{*E}$$
4-11

Where the excess Gibbs free energy associated with the elecNRTL model is given by the following term [46]:

$$\frac{G_m^{*E}}{RT} = \frac{G_m^{*E,PDH}}{RT} + \frac{G_m^{*E,Born}}{RT} + \frac{G_m^{*E,lc}}{RT} + \frac{G_m^{*E,lc}}{RT}$$
 4-12

Where,

PDH is the Pitzer-Debye- Hückel contribution for long range ion-ion interactions, Born is the Born Correction for change in mixed solvent reference state, and lc is the local contribution for short range interactions.

To determine the activity coefficients within the elecNRTL model the following thermodynamic relationship between the excess Gibbs free energy and the activity coefficient is used:

$$ln\gamma_i = \frac{G_m^{*E}}{RT} = \left[\frac{\delta(nG_m^{*E}/RT)}{\delta n_i}\right]$$
 4-13

When applying equation 4-12 to equation 4-13 the following expression for the activity coefficients is obtained:

$$ln\gamma_i^* = ln\gamma_i^{*,PDH} + ln\gamma_i^{*,Born} + ln\gamma_i^{*,lc}$$

$$4-14$$

4.1.3.1 Long-range contribution

The first term in equation 4-12 is the Pitzer-Debye-Hückel long range contribution [47]. This contribution takes into account the interactions that exists beyond the immediate neighborhood of an ionic species and is expressed as follows:

$$\frac{G_m^{*E,PDH}}{RT} = -\sum_k x_k \left(\frac{1000}{M_s}\right)^{0.5} \left(\frac{4A_\phi I_x}{\rho}\right) \ln(1+\rho I_x^{0.5})$$
 4-15

Where,

 M_s is the molecular weight of the solvent, and, ρ is the "Closest approach" parameter.

The Debye-Hückel parameter, A_{φ} , and ionic strength of solvent, I_x , are given by equation 4-16 and 4-17 ,

$$A_{\phi} = \frac{1}{3} \left(\frac{2\pi N_A d_s}{1000}\right)^{0.5} \left(\frac{Q_e^2}{\varepsilon_w kT}\right)^{1.5}$$
 4-16

$$I_x = 0.5 \sum_i x_i z_i^2 \tag{4-17}$$

Where, N_A is Avogadro's number, d_s is the density of the solvent, Q_e is the electron charge, ε_w is the dielectric constant of water, k is the Boltzmann constant, T is the temperature, x_i the molar fraction of component i, and, z_i is the charge of the component i.

4.1.3.2 Born correction

The Born correction term accounts for the change in reference state from the mixed-solvent composition to aqueous solution for the Debye-Hückel term, if the infinite dilution aqueous solution is chosen as the reference state. The following equation is used for this purpose [46]:

$$\frac{G_m^{*E,Born}}{RT} = \left(\frac{Q_e^2}{2kT}\right) \left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w}\right) \sum_i \frac{x_i z_i^2}{r_i} 10^{-2}$$

$$4-18$$

Where,

 ε_s is the dielectric constant of the solvent, and, r_i is the Born radius.

The dielectric constant specifies a component's ability to stabilize an ionic solution. As the dielectric constant increases, the tendency for ions to form and remain as ionic species also increases [48]. The temperature dependent correlation for the dielectric constants is described with the following equation:

$$\varepsilon_i = A_i + B_i \left(\frac{1}{T(K)} - \frac{1}{C_i} \right)$$

$$4-19$$

Where,

 A_i , B_i , C_i are coefficients, which describe the temperature dependency of the dielectric constant for a solvent i.

4.1.3.3 Local contribution

The local contribution term accounts for the local interactions that exist at the immediate neighbourhood of any species. The model assumes that there are three types of local composition interactions. The first type consists of a central molecular species with other molecular species, cationic species, and anionic species in the immediate neighbourhood. Here, local electroneutrality is maintained. The other two

types are based on the like-ion repulsion assumption and have either cationic or anionic species as the central species. They also have an immediate neighbourhood consisting of molecular species and oppositely charged ionic species. Accordingly, the excess Gibbs energy from local interactions for an electrolyte system can be written as follows in Equation 4-20 [46]. The first term is the contribution when a molecule species is at the center, the second is the contribution, when a cationic species is at the center, and the third term is the contribution, when an anionic species is at the center. Subscripts m, c, and a, represent molecules, cations, and anions, respectively.

$$\frac{G_m^{*E,lc}}{RT} = \sum_m X_m \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} + \sum_c X_c \sum_{a'} \left(\frac{X_{a'}}{\sum_{a''} X_{a''}}\right) \frac{\sum_j G_{jc,a'c} \tau_{jc,a'c}}{\sum_k X_k G_{kc,a'c}} + \cdots$$

$$\dots + \sum_a X_a \sum_{c'} \left(\frac{X_{c'}}{\sum_{c''} X_{c''}}\right) \frac{\sum_j G_{ja,a'c} \tau_{ja,a'c}}{\sum_k X_k G_{ka,a'c}}$$
4-20

Where j and k can be any species.

$$\alpha_{cm} = \frac{\sum_{a} X_{a} \, \alpha_{ca,m}}{\sum_{a'} X_{a'}} \qquad \qquad \alpha_{am} = \frac{\sum_{c} X_{c} \, \alpha_{ca,m}}{\sum_{c'} X_{c'}}$$

$$G_{jc,a'c} = \exp(-\alpha_{jc,a'c}\tau_{jc,a'c})$$

$$G_{ja,c'a} = \exp(-\alpha_{ja,c'a}\tau_{ja,c'a})$$

$$G_{im} = \exp(-\alpha_{im}\tau_{im}) \qquad \qquad G_{ca,m} = \exp(-\alpha_{ca,m}\tau_{ca,m})$$

 $\tau_{mc,ca} = \tau_{am} - \tau_{ca,m} + \tau_{m,ca\prime} \qquad \qquad \tau_{mc,ac} = \tau_{cm} - \tau_{ca,m} + \tau_{m,ca\prime}$

 α is the non-randomness parameter

 τ is the binary energy interaction parameter

4.1.3.4 Adjustable model parameters

Summarizing, the adjustable model parameters for the elecNRTL model are the symmetric non-random factor parameters, α , and the asymmetric binary interaction energy parameters, τ . These parameters exist for molecule-molecule pairs ($\alpha_{mm'} = \alpha_{m'm}$ while $\tau_{mm'} \neq \tau_{m'm}$), molecule-electrolyte pairs ($\alpha_{m,ca} = \alpha_{ca,m}$ while $\tau_{m,ca} \neq \tau_{ca,m}$ where ca represents an ion pair), and electrolyte-electrolyte pairs ($\alpha_{ca,ca'} = \alpha_{ca',ca}$ and $\alpha_{ca,c'a} = \alpha_{c'a,ca}$ while $\tau_{ca,ca'} \neq \tau_{ca',ca}$ and $\tau_{ca,c'a} \neq \tau_{c'a,ca}$). The parameters for the ion pairs are temperature dependent:

$$\tau_{m,ca} = C_{m,ca} + \frac{D_{m,ca}}{T} + E_{m,ca} \left[\frac{(T^{ref} - T)}{T} + \ln\left(\frac{T}{T^{ref}}\right) \right]$$
 4-21

$$\tau_{ca,m} = C_{ca,m} + \frac{D_{ca,m}}{T} + E_{ca,m} \left[\frac{(T^{ref} - T)}{T} + \ln\left(\frac{T}{T^{ref}}\right) \right]$$

$$4-22$$

$$\tau_{ca,c'a} = C_{ca,c'a} + \frac{D_{ca,c'a}}{T} + E_{ca,c'a} \left[\frac{(T^{ref} - T)}{T} + \ln\left(\frac{T}{T^{ref}}\right) \right]$$
 4-23

$$\tau_{c'a,ca} = C_{c'a,ca} + \frac{D_{c'a,ca}}{T} + E_{c'a,ca} \left[\frac{(T^{ref} - T)}{T} + \ln\left(\frac{T}{T^{ref}}\right) \right]$$
 4-24

$$\tau_{ca,ca'} = C_{ca,ca'} + \frac{D_{ca,ca'}}{T} + E_{ca,ca'} \left[\frac{(T^{ref} - T)}{T} + \ln\left(\frac{T}{T^{ref}}\right) \right]$$
 4-25

$$\tau_{ca',ca} = C_{ca',ca} + \frac{D_{ca',ca}}{T} + E_{ca',ca} \left[\frac{(T^{ref} - T)}{T} + \ln\left(\frac{T}{T^{ref}}\right) \right]$$

$$4-26$$

Where,

 $T^{ref} = 298$ K, and,

C, D, E are the coefficients, which describe the temperature dependency of the energy parameters.

The temperature dependency of the NRTL parameters used for molecule-molecule parameters is given by:

$$\tau_{ij} = A_{ij} + \frac{B_{ij}}{T} + F \ln T + G_{ij}T$$
 4-27

$$\alpha_{ij} = C_{ij} + D_{ij}(T - T^{ref})$$

$$4-28$$

Table 4-4 the data requirement for the electrolyte NRTL activity coefficient model is summarized.

Physcial	Parameter in
property	Aspen
$A_i, B_i, C_i \text{ for } \varepsilon_i$	CPDIEC(1-3)
r _i	RADIUS
A_{ij} - G_{ij} , α_{ij} , α_{ji}	NRTL(1-6)
$C_{m,ca}$, $C_{ca,m}$, $C_{ca,c'a}$,	GMELCC
$C_{c'a,ca}, C_{ca,ca'}, C_{ca',ca}$	
$D_{m,ca}, D_{ca,m}, D_{ca,c'a},$	GMELCD
$D_{c'a,ca}, D_{ca,ca'}, D_{ca',ca}$	CIIILEE
$E_{m,ca}$, $E_{ca,m}$, $E_{ca,c'a}$,	GMELCE
$E_{c'a,ca}, E_{ca,ca'}, E_{ca',ca}$	GMILLEL
$\alpha_{m,ca}$, $\alpha_{ca,m}$, $\alpha_{ca,c'a}$,	GMELCN
$\alpha_{c'a,ca}, \alpha_{ca,ca'}, \alpha_{ca',ca}$	

Table 4-4. Data requirement for the electrolyte NRTL activity coefficient model.

4.1.4 Pure component ideal gas heat capacity

Depending on the given properties, the ideal gas heat capacity for pure component is calculated with different equations. For AMP the ideal gas heat capacity polynomial is used:

$$C_{p,i}^{*,ig} = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5$$

$$4-29$$

For the other pure components, H_2O , CO_2 and PZ, the DIPPR³ equation by Aly and Lee 1981[49] is used:

$$C_{p,i}^{*,ig} = C_{1i} + C_{2i} \left(\frac{C_{3i}/T}{\sinh(C_{3i}/T)} \right)^2 + C_{i4} \left(\frac{C_{5i}/T}{\cosh(C_{5i}/T)} \right)^2$$

$$for \ C_{6i} \le T \le C_{7i}$$

$$4-30$$

The coefficients used to describe the temperature dependency of the ideal gas heat capacity for AMP, PZ, H_2O and CO_2 are summarized in Table 4-5 and Table 4-6.

Parameter in AMP^1 Coefficient Unit Aspen C_{1i} J/kmol K -3201,44 CPIG-1 J/kmol K C_{2i} CPIG-2 555,596 J/kmol K C_{3i} CPIG-3 -0,369361 C_{4i} CPIG-4 J/kmol K 9,93483E-05 CPIG-5 J/kmol K C_{5i} 0 C_{6i} CPIG-6 J/kmol K 0

Table 4-5. Data requirement for the ideal gas heat capacity polynomial.

Source (Aspen PlusTM databases): ¹ DB-ELECPURE

Table 4-6. Data requirement for the DIPPR equation for the ideal gas heat capacity.

Physical	Parameter in	Unit		CO^{1}	$\mathbf{p}7^{1}$
property	Aspen	Unit	$\Pi_2 O$	CO_2	ΓZ
C _{1i}	CPIGDP-1	J/kmol K	33363	29370	81930
C_{2i}	CPIGDP-2	J/kmol K	26790	34540	236600
C_{3i}	CPIGDP-3	Κ	2610.5	1428	1269.8
C_{4i}	CPIGDP-4	J/kmol K	8896	26400	174500
C_{5i}	CPIGDP-5	K	1169	588	695

³ DIPPR: Design Institute for Physical Properties

C _{6i}	CPIGDP-6	K	100	50	300
C_{7i}	CPIGDP-7	K	2273.15	5000	1500

Source (Aspen PlusTM databases): ¹ DB-PURE28

4.1.5 Pure component enthalpy of vaporization

Depending on the given properties, the heat of vaporization for pure components is calculated with different equations.

For H₂O, CO₂ and AMP, the Watson heat of vaporization equation is used (Equ. 4-31) ([46] p.197). It estimates the heat of vaporization of a pure liquid component at any temperature from the known value at a single temperature $(\Delta H_i(T_1))$.

$$\Delta_{vap} H_i^*(T) = \Delta_{vap} H_i^*(T_1) \left(\frac{1 - T/T_{ci}}{1 - T_1/T_{ci}}\right)^{a_i + b_i(1 - T/T_{ci})} 4-31$$

Where, T_{ci} is the critical temperature, T is the temperature in K.

In Table 4-7 the data requirements for this equation and the coefficients used for H_2O , CO_2 and AMP are summarized.

Table 4-7. Data requirement for the Watson heat of vaporization equation.

Physical	Parameter in	Unit	$H_{2}O^{1}$	CO_{2}^{1}	ΔMP^2	
property	Aspen	Oint	$\Pi_2 O$	CO_2		
$\Delta_{vap}H_i^*(T_1)$	DHVLWT-1	kJ/kmol	40683.1	17165.9	40759	
T_1	DHVLWT-2	K	373.2	194.7	438.65	
a_i	DHVLWT-3	-	0.310646	0.357629	0.38	
$\mathbf{b}_{\mathbf{i}}$	DHVLWT-4	-	0	0	0	
T_{min}	DHVLWT-5	K	273.2	194.7	438.65	

Source (Aspen PlusTM databases): ¹ DB-ASPENCPD, ² DB-ELECPURE

The heat of vaporization for PZ is calculated with the DIPPR heat of vaporization equation:

$$\Delta_{vap}H_i^* = C_{1i}(1 - T_{ri})^{(C_{2i} + C_{3i}T_{ri} + C_{4i}T_{ri}^2 + C_{5i}T_{ri}^3)} \quad \text{for } C_{6i} \le T \le C_{7i}$$

Where, T_{ri} is the reduced temperature T / T_{ci} , T_{ci} is the critical temperature of component i, T is the temperature in K.

In Table 4-8 for PZ the coefficients, which describe the DIPPR heat of vaporization equation, are presented.

Table 4-8. DIPPR heat of vaporization coefficients for PZ.

Coefficient	Parameter in Aspen	Unit	PZ^1
C _{1i}	DHVLDP-1	kJ/kmol	53547
C_{2i}	DHVLDP-2	-	-0,12435
C_{3i}	DHVLDP-3	-	0,63144
C_{4i}	DHVLDP-4	-	-0,13983
C_{5i}	DHVLDP-5	-	0
C _{6i}	DHVLDP-6	K	379,15
C_{7i}	DHVLDP-7	K	638

Source (Aspen PlusTM databases): ¹ DB-PURE28

4.1.6 Aqueous infinite dilution heat capacity model

The aqueous phase infinite dilution enthalpies, entropies, and Gibbs energies are calculated from the heat capacity polynomial. The values are used in the calculation of aqueous and mixed solvent properties of electrolyte solutions:

$$C_{p,i}^{\infty,aq} = C_{1i} + C_{2i}T + C_{3i}T^2 + \frac{C_{4i}}{T}$$

$$4-33$$

The coefficients for all ionic species are given in Table 4-9 and Table 4-10.

Coefficient	Parameter	Unit	<u>ОЦ-</u>			$CO3^{2-}$	D7U+
	in Aspen	Unit	OH	П ₃ О	nco ₃	COS	I ZII
C _{1i}	CPAQ0-1	kJ/kmol K	-148.5	75.29	-29.26	-397.1	193.99
C_{2i}	CPAQ0-2	kJ/kmol K	0	0	0	0	0
C_{3i}	CPAQ0-3	kJ/kmol K	0	0	0	0	0
C_{4i}	CPAQ0-4	kJ/kmol K	0	0	0	0	0

 Table 4-9. Infinite Dilution Aqueous Phase Heat Capacity Coefficients.

Sources (Aspen PlusTM databases): DB-AQUEOUS

 Table 4-10. Infinite Dilution Aqueous Phase Heat Capacity Coefficients continued.

Coefficient	Parameter in Aspen	Unit	PZCOO ⁻	PZ(COO ⁻) ₂	H ⁺ PZCOO ⁻	$AMPH^+$
C _{1i}	CPAQ0-1	kJ/kmol K	302.448	72.038	23.775	559
C_{2i}	CPAQ0-2	kJ/kmol K	0	0	0	410
C_{3i}	CPAQ0-3	kJ/kmol K	0	0	0	0
C_{4i}	CPAQ0-4	kJ/kmol K	0	0	0	0

Sources (Aspen PlusTM databases): DB-AQUEOUS

4.1.7 Henry's constants

The Henry's constants are an important part for the vapor liquid equilibrium of dissolved gases. Henry's law is used to predict the solubility of a gases, such as CO_2 , in the solvent and is applied to molecular solutes in enthalpy and aqueous chemistry algorithms. There are two activity coefficient basis for Henry components, mixed solvent and aqueous. Thus the reference state for the activity coefficient of molecular solutes can be chosen between infinite dilution in a mixed solvent or infinite dilution

in an aqueous solvent⁴. A volume weighted mixing rule is applied to describe the Henry's constant of CO_2 in mixed solvent as shown below [50, 51].

$$\ln\left(\frac{H_i}{\gamma_i^{\infty}}\right) = \sum_A w_A \ln\left(\frac{H_{i,A}}{\gamma_{iA}^{\infty}}\right)$$
 4-34

Where,

$$w_A = \frac{x_A (V_{cA})^{2/3}}{\sum_B x_B (V_{cB})^{2/3}}$$
 4-35

 γ_i^{∞} is the activity coefficient at infinite dilution, w_A is the weight fraction of solvent A, x_A and x_B are the molar fractions of solvent A and B, V_{cA} and V_{cB} are the critical volume of solvent A and B.

The temperature dependent correlation for Henry's constants is described as followed:

$$\ln H_{iA}(T, P_A^{*l}) = C_1 + \frac{C_2}{T(K)} + C_3 \ln T(K) + C_4 T(K) + \frac{C_5}{T(K)^2}$$

$$for T_L \le T \le T_H$$
4-36

Where,

 P_A^{*l} is the vapor pressure of solvent A,

 $\mathrm{C}_1\text{-}\mathrm{C}_5$ are the coefficients, which describe the temperature dependency of the Henry's constant

For temperatures outside the bonds T_L and T_H linear extrapolation occurs for $\ln H_{iA}$.

$$H_{iA}(T,P) = H_{iA}(T,P_A^{*l})exp\left(\frac{1}{RT}\int_{P_A^{*l}}^{P}V_{iA}^{\infty}dp\right)$$
4-37

⁴ This can be specified on the **Setup** | **Calculation Options** | **Reactions** sheet.

Where,

 $exp\left(\frac{1}{RT}\int_{P_A^{*l}}^{P}V_{iA}^{\infty}dp\right)$ is the Henry's constant pressure correction term,

 V_{iA}^{∞} is the partial molar volume of a supercritical component i at infinite dilution in solvent A

For this calculations V_{iA}^{∞} is obtained from the Brelvi-O'Connell model, P_A^{*l} from the extended Antoine model and γ_i^{∞} from the electrolyte NRTL activity coefficient model.

The required data for this model are the coefficients C_1 - C_5 , which describe the temperature dependency of the Henry's constants (expressed in Aspen PlusTM with HENRY1-5).

4.1.8 Brelvi-O'Connell model

The Brelvi-O'Connell model calculates the partial molar volume of a supercritical component i at infinite dilution in pure solvent A. Partial molar volume at infinite dilution is required to compute the effect of pressure on Henry's constant (see Henry's constant) The general form of the Brelvi-O'Connell model is:

$$V_{iA}^{\infty} = fcn(V_i^{BO}, V_A^{BO}, V_A^{*l})$$
 4-38

Where,

 $V^{BO} = V_1 + T V_2$, is the Brelvi-O'Connell parameter V_A^{*l} is the liquid molar volume of solvent A

The above correlation applies to both solute and solvent. The liquid molar volume of solvent is obtained from the Rackett model (see Chapter 4.1.10).

Table 4-11. Parameter requirements for the Brelvi-O'Connell model.

Parameter	Parameter in Aspen	Unit	CO_2	H ₂ O
V_1	VLBROC/1	cum/kmol	0.0939	0.0464
V_2	VLBROC/2	cum/kmol	0	0

Sources (Aspen PlusTM databases): DB-ELECPURE

4.1.9 Clarke Aqueous Electrolyte Volume

The Clarke model calculates the liquid molar volume for electrolyte solutions. For this a liquid volume quadrating mixing rule is applied:

$$V_{m}^{l} = \sum_{i} x_{i} V_{i}^{*,l} + \sum_{j} x_{j} K_{ij} \left(V_{i}^{*,l} V_{j}^{*,l} \right)^{0.5}$$

$$4-39$$

Where,

x is the molar fraction of component i, $V_i^{*,l}$ is the liquid molar volume of component i, and, K_{ij} is a binary interaction parameter.

For this calculations $V_i^{*,l}$ is obtained from the Rackett equation. The data requirement and the used values for the components H₂O, AMP and PZ are summarized in Table 4-12.

 Table 4-12. Parameter requirements for the Clarke aqueous electrolyte volume.

Kij (VLQKIJ)	H ₂ O	PZ	AMP
H ₂ 0	-	-0.198022	-0.122353
PZ	-0.198022	-	0*
AMP	-0.122353	0*	-

Sources: Aspen PlusTM example *default value

4.1.10 Rackett equation

The Rackett equation is used to predict the density of a pure liquid dependent on temperature based on its critical properties. One density value is required to calculate the Rackett constant in the equation. Then the critical properties TC, VC and PC are used to estimate new density values as the temperature changes.

$$V_i^{*l} = \frac{RT_{cA} Z_A^{RA[1+(1-TcA)^{2/7}]}}{p_{cA}}$$
 4-40

The parameter requirements and the used values are summarized in Table 4-13.

Parameter	Parameter in Aspen	Unit	AMP^1	PZ^2	H_2O^2	$\mathrm{CO_2}^2$
T _{cA}	TC	K	635	638	647	304
p_{cA}	PC	kPa	4862.97	5530	22064	7383
Z_A	RKTZRA	-	0.2671614	-	0,243172	0,27256

 Table 4-13. Parameter requirements for the Rackett equation.

Sources (Aspen PlusTM databases): ¹ DB-ELECPURE, ² DB-PURE28

4.1.11Extended Vapor Pressure Correlation

For the description of the vapor pressures the extended Antoine equation is applied. It describes the relation between the vapor pressure and temperature for pure components:

$$\ln P_i^{*l}\left(\frac{N}{m^2}\right) = A + \frac{B}{T(K) + C} + DT(K) + E\ln T(K) + FT(K)^G$$
 4-41

Ionic species are defined as non-volatile components. For this A is set to -1E+20 and the remaining parameters to zero. In Aspen PlusTM the parameter PLXANT(1-7) describes the coefficients A-G of the temperature dependent correlation.

4.1.12Aqueous phase chemistry

Each chemical equilibrium in the liquid phase is characterized by a chemical equilibrium constant. The chemical equilibrium constants are expressed in Aspen Plus in terms of the activity of component i in the jth reaction:

$$K_j = \prod_i \alpha_i^{\nu_i} = \prod_i (x_i \gamma_i)^{\nu_i}$$
 4-42

Where, K_j is the chemical equilibrium constant, α_i is the activity, v_i is the reaction stoichiometric coefficient of component i, x_i is the mole fraction of component i, and, γ_i is the activity coefficient of component i

There are two options how to define the chemical equilibrium constants. On option is to describe the equilibrium constants by its temperature dependent function. The temperature dependency of the equilibrium constants defined in mole-fraction scale is expressed by Equation 4-43.

$$\ln K = a + \frac{b}{T} + c \ln T + dT$$
4-43

Another option is to calculate the equilibrium constants in terms of the reference state Gibbs free energy of the system as expressed in the following equation:

$$\ln K_j = -\frac{\Delta G_{i,j}^0}{RT}$$
 4-44

Where, $\Delta G_{i,j}^0$ is the reference state Gibbs free energy, R is the ideas gas constant.

The framework allows the rigorous thermodynamic model to be internally consistent with respect to governing thermodynamic definitions. The equation used for those calculations is:

$$-\ln K_{j} = \frac{\Delta G_{m}^{0}}{RT} = \frac{\Delta G_{m}^{0} - \Delta H_{0,m}^{0}}{RT_{0}} + \frac{\Delta H_{0,m}^{0}}{RT} + \frac{1}{T} \int_{T_{0}}^{T} \frac{\Delta C_{p,m}^{0}}{R} dT - \int_{T_{0}}^{T} \frac{\Delta C_{p,m}^{0}}{R} \frac{dT}{T}$$
 4-45

A detailed mathematical derivation of this relation for the calculation of the equilibrium constants calculations in Aspen PlusTM can be found in [48].

4.2 Vapor phase

The vapor phase is represented by Soave's modification of the Redlich-Kwong equation [52]. This equation-of-state can be used for hydrocarbon systems that include the common light gases, such as H_2S , CO_2 and N_2 . The Soave-Redlich-Kwong equation is given by the following expression:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b)}$$

$$4-46$$

Where V_m is the molar Volume, a is the energy parameter, and, b the size parameter.

$$a = a_0 + a_1$$

 a_0 is the standard mixing quadratic term:

$$a_0 = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - k_{ij})$$

a₁ is an additional, asymmetric (polar) term:

$$a_{1} = \sum_{i=l}^{N} \left(\sum_{j=l}^{Z} x_{j} \left(\left(a_{i}a_{j} \right)^{0.5} l_{i,j} \right)^{1/3} \right)^{3}$$
$$b = \sum_{i} x_{i}b_{i}$$
$$k_{ij} = k_{ji}$$

$$a_{i} = \alpha_{i} 0.42747 \frac{R^{2} T_{c_{i}}^{2}}{P_{c_{i}}}$$

$$\alpha_{i} = \left[1 + m_{i} \left(1 - T_{r_{i}}^{0,5}\right)\right]^{2}$$

$$m_{i} = 0.48 + 1.57 \omega_{i} - 0.176\omega_{i}^{2}$$

$$b_{i} = 0.08664 \frac{RT_{c_{i}}}{P_{c_{i}}}$$

x is the molar fraction, $l_{i,j}$ and k_{ij} are binary interaction parameter, T_c is the critical temperature, P_c is the critical pressure, T_r is the reduce temperature; $T_r = T/T_c$, ω_i is the acentric factor.

Where,

With this model the physical properties such as enthalpy, Gibbs free energy, Entropy, density and vapor fugacity coefficient are calculated based on fundamental thermodynamic relations [35].

The data requirement and the used values are summarized in Table 4-14.

Fable 4-14. Parameter require	irements for Soave	-Redlich-Kwong	equation of state
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Parameter	Parameter in Aspen	Unit	AMP ¹	PZ^2	H_2O^2	CO_2^2
T_c	TC	K	635	638	647	304
P_c	PC	kPa	4862.97	5530	22064	7383
ω_i	OMEGA	-	0.793327	0.41376	0.344861	0.223621
kij	SRKKIJ	-	0*	0*	0*	0*
$l_{i,j}$	SRKLIJ	-	0*	0*	0*	0*

Sources (Aspen PlusTM databases): ¹ DB-ELECPURE, ² DB-PURE28 *default value

4.3 Vapor-liquid equilibrium calculations

When the physical properties are calculated the equilibrium between the vapor and liquid phase can be calculated. At equilibrium condition the fugacity of each component in liquid and vapor phase must be equal:

$$f^{\nu} = f^l \tag{4-47}$$

Equation 4-48 describes the vapor-liquid equilibrium for non-Henry component species [53]:

$$y_i \hat{\phi}_i^v P = x_i \gamma_i \hat{\phi}_i^0 P_i^0 exp\left[\frac{V_i^l (P - P_i^0)}{RT}\right]$$

$$4-48$$

Where,

 y_i and x_i are the molar fractions in vapor and liquid phase respectively,

P and T are the system pressure and temperature,

R is the ideal gas constant,

 $\hat{\phi}_i^{\nu}$ the vapor fugacity coefficient of component i in the mixture,

 γ_i is the activity coefficient of component i in the mixture,

 $\hat{\phi}_i^0$ liquid pure component fugacity coefficient of component i,

 P_i^0 pure component saturation pressure for component i,

 $exp\left[\frac{V_i^l(P-P_i^0)}{RT}\right]$ is the pointing correction factor, and,

 V_i^l is the partial liquid molar volume of component i.

And the vapor-liquid equilibrium for Henry components can be described with Equation 4-49 [53]:

$$y_i \hat{\phi}_i^{\nu} P = x_i \gamma_i \left(\frac{H_i}{\gamma_i^{\infty,aq}}\right) exp\left[\frac{V_i^{\infty,aq}(P - P_i^0)}{RT}\right]$$

$$4-49$$

Where,

 H_i is the Henry's constant for component i,

 $\gamma_i^{\infty,aq}$ is the infinite dilution activity coefficient for component, $V_i^{\infty,aq}$ is the Brevi-O'Connell partial molar volume for component i.

The vapor-liquid equilibrium is calculated based on an iterative algorithm, since the activity coefficients and fugacity coefficients are dependent on the concentration. The models and equations used for the calculation of the physical properties, which participate in the vapor-liquid equilibrium calculations, are shown in Table 4-15.

Physical Property	Model/equation
$\widehat{\phi}_i^ u$	Soave-Redlich-Kwong
γ_i	Electrolyte NRTL activity coefficient model
$\widehat{\phi}_{i}^{0}$	Soave-Redlich-Kwong
P_i^0	Extended Antoine
V_i^l	Rackett equation
H_i	Henry's law
$\gamma_i^{\infty,aq}$	Electrolyte NRTL activity coefficient model
$V_i^{\infty,aq}$	Brevi-O'Connell model

 Table 4-15. Models and equations used for the calculations of the physical properties

 participating in the VLE calculations.

4.4 Data requirement for the elecNRTL model

In Table 4-16 the data requirement for the models and equations applied in the elecNRTL model is summarized. The requirements are divided into pure component properties, binary interaction parameters and electrolyte interaction parameters.

Physical property	Parameter in	Molecules	Molecular solutes	Ions	
	Aspen				
	Pure con	mponent prope	rties		
$C_{p,i}^{\infty,aq}$	CPAQ0(1-4)			Х	
A_i, B_i, C_i for ε_i	CPDIEC(1-2)	Х			
$C^{*,ig}$	CPIG(1-6)/	v	v		
$c_{p,i}$	CPIGDP(1-7)	Α	А		
$\Delta_f G_k^{\infty,aq}$	DGAQFM		х	Х	
$\Delta_f G_w$	DGFORM	Х			
$\Delta_{f}H_{k}^{\infty,aq}$	DHAQFM		Х	Х	
$\Delta_{f} H^{*,ig}_{w}$	DHFORM	Х			
۸ ۲۲*	DHVLWT(1-7)/				
$\Delta_{vap}H_i$	DHVLDP(1-5)	Х			
ω_i	OMEGA	Х	Х		
p_{cA}	PC	Х	Х		
P_i^{*l}	PLXANT(1-7)	Х	х	Х	
r_{i}	RADIUS			Х	
Z_A	RKTZRA	Х	Х		
T_{cA}	TC	Х	Х	Х	
	Binary in	teraction paran	neters		
H _{iA}	HENRY(1-5)	Х	Х		
A_{ij} - $G_{ij}, \alpha_{ij}, \alpha_{ji}$	NRTL(1-6)	Х	Х		
V ₁ ,V ₂	VLBROC-1,2	Х	х	Х	
Kij	VLQKIJ	Х	Х	Х	
Electrolyte interaction parameters					
$C_{m,ca}$, $C_{ca,m}$,					
$C_{ca,c'a}, C_{c'a,ca},$	GMELCC	Х	Х	Х	
$C_{ca,ca\prime}, C_{ca\prime,ca}$					

Table 4-16. Data requirement for the elecNRTL model for molecules, molecular solutes and ions.

D _{m,ca} , D _{ca,m} , D _{ca,c'a} , D _{c'a,ca} , D _{ca,ca} , D _{ca',ca}	GMELCD	х	Х	х
$E_{m,ca}$, $E_{ca,m}$, $E_{ca,c'a}$, $E_{c'a,ca}$, $E_{ca,ca'}$, $E_{ca',ca}$	GMELCE	Х	х	х
$lpha_{m,ca}$, $lpha_{ca,m}$, $lpha_{ca,c'a}$, $lpha_{c'a,ca}$, $lpha_{ca,ca'}$, $lpha_{ca',ca}$	GMELCN	Х	Х	Х

5 Modeling procedure in Aspen PlusTM

In this chapter the modeling procedure of amine solvents using the elecNRTL model is described. First a general procedure for multicomponent blended amine solvents is presented. Afterwards an approach for the application of the modeling procedure to any amine solvent is suggested.

5.1 General procedure for the modeling of blended amine solvent system in Aspen PlusTM

When modeling an electrolyte solvent system using the elecNRTL model the required data for this model such as pure component physical properties, binary interaction parameters and electrolyte pair interaction parameters need to be provided as described in Chapter 4.

In a first step the physical scalar and temperature dependent properties for each molecular component, molecular solute and ion have to be determined, if they are not available in one of the Aspen PlusTM, NIST or DECHEMA databases. As described in Chapter 2, there is the possibility to estimate the properties for molecular components with group contribution methods implemented in Aspen PlusTM based on the molecular structure of the molecules. Thereby the accuracy of the estimated properties has to be considered carefully. Another option is the regression of experimental pure component physical property data using the Data Regression System (DRS) in Aspen PlusTM. With this tool various types of pure component physical property parameters can be fit to experimental data. Since those parameters represent pure components properties, they are determined without respect to other participating components in the solvent system.

When all pure component properties are determined, the binary and electrolyte pair interaction parameters have to be provided. Depending on the composition of the multicomponent solvent system those parameters may not be available in the Aspen Plus databases. Those parameters can be regressed with the DRS in Aspen PlusTM as well. As the name "binary interaction parameters" and "electrolyte pair interaction

parameters" says, those parameters describe interactions between two components or component pairs. Due to this reason a tier approach is applied for the regression of those parameters to regress those step by step. Within this tier approach the solvent system is divided into its thermodynamic sub-component systems. Following the example of the quaternary system of PZ-AMP-H₂O-CO₂, these ones are AMP-H₂O-CO₂, PZ-H₂O-CO₂, AMP-H₂O and PZ-H₂O as can be seen in Figure 5-1.



Figure 5-1. Thermodynamic sub-component systems of the system PZ-AMP-H₂O-CO₂

The interaction parameters are regressed to fit VLE data for each system. Following this tier approach, first the binary interaction parameters for the secondary systems are regressed. In the next step those regressed interaction parameters are fixed and the complementary interaction parameters for the ternary system are regressed with VLE data for the ternary system and so on. For a better understanding Figure 5-2 visualizes this modeling procedure following the examples for the quaternary system PZ-AMP- H_2O-CO_2 . This approach assures a higher accuracy and limits the parameter variance during the regression.



Figure 5-2. Modeling approach for the quaternary system AMP-PZ-H₂O-CO₂.

5.1.1 Parameter regression

For parameter regression a data regression system (DRS) is implemented in Aspen PlusTM. It can be used to fit various types of pure component physical property data such as vapor pressure etc., but its primary use is to customize thermodynamic models dealing with vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE) [54]. Experimental vapor-liquid equilibrium data can be regressed to obtain parameters, which describe the selected thermodynamic model. The adjustable parameters of the elecNRTL model are described in Chapter 4.

In this work only the regression of the binary and electrolyte pair interaction parameters is described. The data set used for VLE data in Aspen PlusTM is called

TPXY for temperature (T), pressure (P), liquid mole fraction (X) and vapor mole fraction (Y), respectively. This data set requires information about temperature, total system pressure, liquid phase concentration and vapor phase concentration. In literature the CO₂ solubility data (VLE data) is normally reported as equilibrium partial pressure of CO₂ over the loading of CO₂ absorbed in the solvent. Thus the total vapor pressure is not known. To implement these data into the TPXY data set, the mole fraction of CO₂ in the vapor phase is set to one. Then, under the input sheet constraints amines and water are cleared to only leave CO₂. This way, the total vapor pressure is equivalent to the equilibrium partial pressure of CO₂ [55] and the TPXY data set can be used.

For the regression not all existing parameters are chosen for regression. Just interaction parameters with physical significance should be selected. One indicator for the physical significance is the speciation of the liquid phase. Components with a higher concentration affect the behavior of the solution more than components with a lower concentration.

For the initial values of the regression parameters default values suggested by Chen and Evans (1986) [56] should be used (see Table 5-1).

 Table 5-1. Default electrolyte pair interaction parameters for the elecNRTL model

 suggested by Chen and Evans (1986) [56].

Parameter	C _{m,ca}	C _{ca,m}	D _{m,ca}	D _{ca,m}	α_{ij}
τ (H2O - ion pair)	8.045	-4.072	0.0	0.0	0.2
τ (CO2 - ion pair)	15.0	-8.0	0.0	0.0	0.2
τ (molecule - ion pair)	10.0	-2.0	0.0	0.0	0.2

During the parameter regression the following points have to be considered to conduct a successful regression:

1. All of the data is reasonable and does not contain outliers.

The data should be accurately measured or taken from a reliable source. To remove clear outliners, the data can be plotted and visually assessed. Data points, which deviate conspicuously from the other data points, should be removed.

2. The best model is used (activity model, equation of state).

To make sure, that a suitable thermodynamic model is selected, the "Property Method Selection Assisstant" in Aspen PlusTM can be used. This tool helps to select the most appropriate property method based on questions about the component system or process type. Additionally the review of literature about modeling of the present or a similar component system can be useful to support the decision.

3. The number of parameters regressed is reasonable - not too few or too many.

It is difficult to generalize the number of parameters, that is reasonable for the regression. As stated above, just parameters with physical significance should be selected for regression. Besides this, it is also depending on the amount of data used for the regression. A way to find out can be the validation of regression results containing different numbers of parameters.

5.2 Application of the modeling procedure to a given amine solvent system

For the application of the presented modeling procedure three steps are suggested to be followed for the application to an arbitrary solvent system. These three steps help to apply the modeling procedure to any amine solvent system, with different states of data availability.
1. Review of available data

In the first step the available pure component physical property data and interaction parameters following the list presented in Table 4-16 are reviewed and the availability of existing subcomponent models is checked.

2. Validation of available data

In a second step, the available parameters and models of the subcomponent systems need to be validated, to assess the accuracy of those models and make a decision, whether the data accuracy is sufficient.

3. Regression of required complementary parameters

In the third step the required complementary parameters are regressed following the regression procedure described in Chapter 5.1.

4. Model validation

To check, whether the regression works and delivers reasonable results, the model is validated with available experimental data.

6 Modeling of the quaternary PZ-AMP-H₂O-CO₂ solvent system

In this chapter the modeling of the quaternary PZ-AMP-H₂O-CO₂ solvent system is presented. In the first section the selected solvent system is described in more detail including the chemical and vapor-liquid equilibrium and special characteristics of the solvent system, which need to be considered during the modeling. In the following sections the modeling is performed following the four steps described in Chapter 5.2.

6.1 Quaternary system: PZ-AMP-H₂O-CO₂

The quaternary system PZ-AMP- H_2O-CO_2 is a blended amine system combining advantages of AMP and PZ. The sterically hindered amine AMP is recommended for its high CO_2 loading capacity and ease of regeneration at low temperatures [57]. However, it shows a very slow reaction rate. To compensate for this, PZ is added, which acts as promoter to improve the CO_2 mass transfer rates [16].

6.1.1 Chemical and vapor-liquid equilibrium

Figure 6-1 illustrates the chemical and vapor-liquid equilibrium for the quaternary system PZ-AMP-H₂O-CO₂. Reactions 1 to 9 (R1-R9) describe the chemical reactions taking place in the liquid phase. The first reaction describes the dissociation of water into oxonium ions (H₃O⁺) and hydroxide ions (OH⁻). The second and third reaction describe the dissociation of carbon dioxide (CO₂) to bicarbonate and the further dissociation to carbonate, respectively. Reactions 4 to 7 involve the reactions related to PZ. Reaction 4 describes the protonation of PZ to protonated PZ (PZH⁺), reaction 5 the PZ carbamate formation (PZCOO⁻), reaction 6 the protonated PZ carbamate formation (PZ(COO⁻)₂). Reaction 8 and 9 involve the reactions related to AMP, whereas reaction 8 describes the protonation of AMP to protonated AMP (AMPH⁺) and reaction 9 the AMP carbamate formation (AMPCOO⁻).



Figure 6-1. Chemical and vapor-liquid equilibrium of the system PZ-AMP-H₂O-CO₂

6.1.2 Special characteristics to be considered

The system $PZ-H_2O-CO_2$ is reported to be difficult to model due to his high number of reactions and the presence of the zwitterion (see 6.1.1). Especially the handling of the zwitterion appears to be challenging. Aspen $Plus^{TM}$ suggests to define the zwitterion as follows:

• Components of type Conventional, similar to solvents

- Parameter ZWITTER set to 1; all other components in the Aspen Physical Property System default to zero for ZWITTER
- Parameter PLXANT/1 less than -1.0E20 so that they are non-volatile.

When defining the zwitterion like this it is going to be handled as follows:

- A zwitterion interacts with other molecular species through NRTL parameters only, excluding any interactions through Henry constants and pair parameters
- The activity coefficient is calculated as a solvent
- The contribution from zwitterions to the solution enthalpy and Gibbs free energy are calculated as solutes using the infinite dilution heat capacity model CPAQ0, DGAQFM, and DHAQFM.

However, in literature and also some Aspen $Plus^{TM}$ example models you see a different handling of zwitterions. For example Hilliard [48] defines the protonated PZ carbamate (H⁺PZCOO⁻) as cation with a charge of 1⁻⁵ in his work, to circumvent the restriction, that the zwitterion is excluded from the molecule/ion interactions, which can cause problems associated with the description of the chemical equilibrium [48]. In the Aspen PlusTM example model for PZ-H₂O-CO₂, which is used in this work, the same zwitterion handling as in Hilliards work is given.

6.2 Step 1: Review of available data

As already shown in Chapter 4.1 and 4.2 all required pure component physical properties are available for the participating species. Additionally there are complete sets of interaction parameters for the two sub-component systems, PZ-H₂O-CO₂ and AMP-H₂O-CO₂, and the complete PZ-AMP-H₂O-CO₂ solvent system [28-31]. That data is summarized in Appendix C Table C - 1 to Table C - 28. Besides this there are Aspen PlusTM example models of the two sub-component systems [58, 59] available as mentioned in Chapter 3.3.3. Due to this high data availability there is no need for the regression of pure component physical properties. Note that the regression of the

interaction parameters for the sub-component systems can be unnecessary, if the available parameters/models represent thermodynamic models with good accuracy.

6.3 Step 2: Validation of available data

In the second step, the available interaction parameters/models of the subcomponent systems are validated, to assess the accuracy of those models. The pure component physical property data is not validated particularly, since this cannot be done within the time scope of this work.

To validate the thermodynamic vapor-liquid equilibrium models of solvent systems for chemical absorption CO_2 capture, certain characteristic parameters are important to assess the ability of the solvent to capture CO_2 . For the validation of the equilibrium conditions of the solvent systems the following properties are used for validation:

- CO₂ partial pressure
- Speciation
- Heat of absorption
- Amine volatility

For the thermodynamic models in Aspen PlusTM, a sensitivity flash curve analysis with a varying CO₂ loading in the solvent (α_{CO2}) is conducted to validate the equilibrium conditions. In Figure 6-2 the flowsheet used for the sensitivity analysis is shown.



Figure 6-2. Flowsheet set up for the sensitivity analysis.

The CO₂ loading in the solvent can be expressed as follows:

$$\alpha_{CO_2} = \frac{n_{CO_2} - n_{CO_2}^g}{n_{amine}} \tag{6-1}$$

Where n_{CO2} is the total amount of moles of CO_2 , n_{CO2}^g the moles of CO_2 in the gaseous phase and n_{amine} the moles of amine in the solvent. To report α_{CO2} in Aspen PlusTM the stream property ML-LOAD is chosen. It reports the ratio of the sum of apparent molar flow rates for the specified components, CO_2 and its derivatives, to the sum of apparent molar flow rates for the base components, PZ, AMP or PZ-AMP and their derivatives.

If the literature data used for validation is not reported in numbers but in diagrams, the software *Datathief* [60] is used to extract the data from the publications into MS Excel.

✤ Equilibrium partial pressure of CO₂

The validation of the equilibrium partial pressure of CO_2 over the loading of CO_2 in the solvent gives information about the equilibrium concentrations in the liquid and vapor phase of the system. It shows how much CO_2 can be absorbed in the solvent at a certain temperature and pressure. To report the CO_2 partial pressure from the outgoing vapor stream of the flash the stream property PPMX is used.

* Speciation

The speciation of the liquid phase gives information about the concentration profile of each species at certain loadings of CO_2 in the solvent. The concentration profile refers to the calculated activity coefficients, which are used to estimate the liquid phase equilibrium. For the validation of the equilibrium liquid phase concentration either the mole flow of the occurring species in the liquid phase or the molar fraction is reported, depending on the literature data used for validation.

✤ Heat of absorption

The enthalpy or heat of absorption (ΔH_{abs}) is an important parameter, which describes the energy released during the chemical absorption process. It also represents the thermal energy required to reverse the reaction and release the CO₂ from the solution. In the flash, the block parameter QCAL expresses the heat of absorption in kJ per sec. To get the heat of absorption per CO₂ absorbed, QCAL is divided by the mole flow of CO₂ absorbed (loading * amine in solution).

♦ Amine volatility

The amine volatility is an important criterion for amines to be used in CO_2 capture, because excessive volatility may result in significant economic losses and environmental impact. To validate the predicted equilibrium amine volatility the stream property PPMX is used for the outgoing vapor stream.

6.3.1 Ternary system: PZ-H₂O-CO₂

In this section two models for the ternary subcomponent system $PZ-H_2O-CO_2$ are validated. The first model is developed based on the physical properties and interaction parameters for the eNRTL model reported by Dash et al. [29] (see Chapter 6.2). The second model is taken from the Aspen PlusTM example database. This database offers a hugh variety of examples for process models including a model for the PZ-H₂O-CO₂ solvent system [59].

6.3.1.1 Dash's work

For the validation of the parameters for the $PZ-H_2O-CO_2$ solvent system by Dash an elecNRTL model is developed in Aspen $Plus^{TM}$ based on the reported values from his work. In the following section the model predictions of the developed model are compared to the reported model predictions by Dash.

Figure 6-3, Figure 6-4 and Figure 6-5 show the comparison of the model predictions for the equilibrium partial pressure of CO_2 over the loading of CO_2 in the solvent for different concentrations and temperatures with Dash's model predictions. In all three figures Dash's predictions for the equilibrium partial pressure of CO_2 cannot be reproduced with the reported physical properties and interaction parameters. Not only the values are not comparable, but also the shape of the model curves is not the same and also no reasonable behavior for a change in temperature and concentration.

Although the comparison of the equilibrium partial pressure of CO_2 is completely off range, the comparison of the model predictions for the speciation shows a quite good accuracy as can be seen in Figure 6-6. In the range of lower loadings, especially for the components AMP, AMPH⁺ and PZ(COO⁻)₂, the fit is better than for higher loadings of CO₂ the deviation from Dash's model prediction increases.

The comparison of the model predictions of heat of absorption for different temperatures is shown in Figure 6-7. The model predictions form the reproduced model deviate significantly from Dash's model predictions.

Figure 6-8 shows the model predictions for the equilibrium partial pressure of PZ over temperature for different CO_2 loadings. The comparison with the model predictions from Dash shows, that the predictions for a loading of 0.188 and 0.688 mol CO_2 per mol AMP fit quite well to Dash's predictions within a certain accuracy. However, for a loading higher than 0.438 mol CO_2 per mol PZ the predictions are completely of as can be seen for the loading of 0.688 mol CO_2 per mol PZ. For even higher loadings it is not possible to make any prediction.



Figure 6-3. Model predictions for the equilibrium partial pressure of CO_2 over the loading of CO_2 in an aqueous solution of 0.2 M PZ for 298 K compared to the model predictions from Dash [29].



Figure 6-4. Model predictions for the equilibrium partial pressure of CO_2 over the loading of CO_2 in an aqueous solution of 0.2 M, 0.8 M and 3.2 M PZ for 328 K compared to the model predictions from Dash [29].



Figure 6-5. Model predictions for the equilibrium partial pressure of CO_2 over the loading of CO_2 in an aqueous solution of 0.6 M PZ for 298 K, 313 K and 343 K compared to the model predictions from Dash [29].



Figure 6-6. Model predictions for the equilibrium liquid phase concentration over the loading of CO2 in an aqueous solution of 3.2 M PZ for 328 K compared to the model predictions from Dash [29].



Figure 6-7. Model predictions for the heat of absorption over the loading of CO₂ for an aqueous solution of 3.2 M PZ for 328 K compared to the model predictions from Dash [29].



Figure 6-8. Model predictions of the equilibrium partial pressure of PZ over the temperature in an aqueous solution of 3.2 M PZ for CO₂ loadings compared to the model results from Dash [29].

6.3.1.2 Aspen PlusTM example

In the following the Aspen $Plus^{TM}$ example for the $PZ-H_2O-CO_2$ solvent system is validated against experimental data and model predictions from literature.

In Figure 6-9, Figure 6-10 and Figure 6-11 the model predictions for the equilibrium partial pressure of CO_2 over the CO_2 loading in the solvent for different amine concentrations and temperatures are compared to experimental data from different sources (see Table 6-1).

[PZ]	Temperature	Data points	Source	
(mol/dm^3)	(K)	Data points	Source	
0.2, 0.6	298 - 343	58	Derks	
0.6	313 - 343	34	Bishnoi and Rochelle	
2	313 - 393	24	Ermatchkov	
4	353 - 393	18	Ermatchkov	
2	313 - 333	14	Hilliard	
0.2, 0.4, 0.8,	208 228	> 100	Dash	
1.6, 3.2, 4.5	298 - 328	> 100	Dasn	

Table 6-1. For validation used VLE data for the ternary system PZ-H₂O-CO₂.

In Figure 6-9 and Figure 6-10 the model shows quite good accuracy to the experimental data by Derks [61], Bishnoi and Rochelle [62], Hilliard [48] and Ermatchkov [63]. The data of the different sources is comparable at given temperatures and concentrations. The experimental data from Derks accord more or less with the data from Bishnoi and Rochelle and Hilliards data with the one from Ermatchkov. However, the comparison of the model predictions with the experimental data from Dash does not show such a good accordance. Especially for increasing loadings of CO_2 and temperature, the model predictions deviate significantly from his data. This fact is further discussed in Chapter 6.3.3.

In Figure 6-12, Figure 6-13, Figure 6-14 and Figure 6-15 the model predictions for the liquid phase concentration over the CO_2 loading in the solvent for different amine concentrations and temperatures are compared to liquid phase concentration model

predictions from different sources. Considering all figures, no comparison shows a very accurate fit for all species. The best overall fit concerning all species is given in the comparison with the data from Kamps. In Figure 6-14 for PZ and its carbamates, $PZCOO^{-}$ and $PZ(COO^{-})_2$, a very accurate fit to the data from Cullinane can be observed, whereas the predictions for PZH^+ and H^+PZCOO^- within the same comparison show high deviations. The highest deviations can be seen in the comparison with Dash's model predictions.

Note as well, that the liquid phase concentration predictions from the different sources differ a lot. Although, the predictions of the CO_2 equilibrium partial pressure show quite good accordance with Hilliard's VLE data (see Equilibrium partial pressure of CO_2), a quite large deviation for the liquid phase concentration can be observed. Based on this, it can be assumed that the accuracy of the predictions for the concentration of each species are either not so important for the CO_2 partial pressure or compensate each other.

In Figure 6-16 and Figure 6-17 the predictions for the heat of absorptions over the loading of CO_2 in the solvent are compared for different concentrations and temperatures with experimental data from Svensson [64] and Hilliard [48]. A Comparinson of both figures shows, that the model predicts more accurate the data from Svensson with an average deviation of about 5 kJ per mol CO_2 . The comparison to Hilliard's data shows roughly an average deviation of about 10 kJ per mole of CO_2 . Besides this, it can be observed, that the experimental data from Hilliard is deviating in a range of about 10 to 15 kJ per mole of CO_2 . That indicates difficulty of the experimental determination of the heat of absorption. Summarizing, the model predicts higher heat of absorptions than measured by Svensson and Hilliard.

In Figure 6-18, Figure 6-19 and Figure 6-20 predictions for the amine volatility over the loading of CO_2 in the solution for different concentration and temperatures is compared to experimental data from Hilliard [48] and Frailie [65]. In all comparisons it can be seen that the predictions for the PZ volatility are significantly higher than experimental data.



Figure 6-9. Model predictions for the equilibrium partial pressure of CO_2 over the loading of CO_2 in an aqueous solution of 0.6 M PZ for 298 K, 313 K and 343 K compared to exp. data from Derks [61] and Bishnoi and Rochelle [62].



Figure 6-10. Model predictions for the equilibrium partial pressure of CO_2 over the loading of CO_2 in an aqueous solution of 2.0 M PZ for 313 K, 333 K, 353 K and 393 K compared to exp. data from Hilliard [48] and Ermatchkov [63].



Figure 6-11. Model predictions for the equilibrium partial pressure of CO_2 over the loading of CO_2 in an aqueous solution of 0.2 M, 0.8 M, 1.6 M and 3.2 M PZ for 328 K compared to exp. data from Dash [29].



Figure 6-12. Model predictions for the liquid phase concentration over the loading of CO₂ in an aqueous solution of 4.0 M PZ for 353 K compared to model predictions from Kamps [66].



Figure 6-13. Model predictions for the liquid phase concentration over the loading of CO₂ in an aqueous solution of 1.0 M PZ for 298 K compared to model predictions from Hilliard [48].



Figure 6-14. Model predictions for the liquid phase concentration over the loading of CO₂ in an aqueous solution of 1.8 M PZ for 333 K compared to model predictions from Cullinane [67].



Figure 6-15. Model predictions for the liquid phase concentration over the loading of CO₂ in an aqueous solution of 3.2 M PZ for 328 K compared to model predictions from Dash [29].



Figure 6-16. Model predictions for the heat of absorption over the loading of CO_2 in an aqueous solution of 2.7 M PZ for 313 K and 318 K compared to exp. data from Svensson [64].



Figure 6-17. Model predictions for the heat of absorption over the loading of CO₂ in an aqueous solution of 2.4 M PZ for 313 K and 353 K compared to exp. data from Hilliard [48].



Figure 6-18. Model predictions for the PZ volatility over the loading of CO₂ in an aqueous solution of 0.9, 2.0, 2.5, 3.6 and 5.0 M PZ for 313 K compared to exp. data from Hilliard [48].



Figure 6-19. Model predictions for the PZ volatility over the loading of CO₂ in an aqueous solution of 0.9, 2.0, 2.5, 3.6 and 5.0 M PZ for 333 K compared to exp. data from Hilliard [48]



Figure 6-20. Model predictions for the PZ volatility over the loading of CO_2 in an aqueous solution of 8.0 M PZ for 313 and 333 K compared to exp. data from Frailie [65].

6.3.2 Ternary system: AMP-H₂O-CO₂

6.3.2.1 Dash's work

For the validation of the AMP-H₂O-CO₂ solvent system by Dash an elecNRTL model is developed in Aspen PlusTM based on the reported values from his work (see Appendix C). In the following text the model predictions of the developed model are compared to the reported model predictions by Dash.

Figure 6-21 and Figure 6-22 show the comparison of the model predictions for the equilibrium partial pressure of CO_2 over the loading of CO_2 in the solvent for different concentrations and temperatures with Dash's model predictions. In both figures the model predictions are comparable for small CO_2 loadings up to 0.5 mol CO_2 per mol AMP. With increasing CO_2 loadings the predictions from the reproduced model deviate significantly from Dash's predictions.

Figure 6-23 shows the comparison of the predictions for the liquid phase concentration over the loading of CO_2 in an aqueous solution of 3.4 M AMP for 328 K with Dahs's predictions.

The comparison of the model predictions of heat of absorption for different temperatures is shown in Figure 6-7. The model predictions from the reproduced model are not consistent with the predictions from Dash.

Figure 6-25 shows the model predictions for the equilibrium partial pressure of AMP over CO_2 loading for different temperatures. The comparison with the model predictions from Dash shows very good accordance, especially for lower temperatures. With increasing temperature the predictions start to deviate for higher CO_2 loadings.



Figure 6-21. Model predictions for the equilibrium partial pressure of CO_2 over the loading of CO_2 in an aqueous solution 3.4 M AMP for 313 K, 318 K and 323 K compared to the model predictions from Dash [31].



Figure 6-22. Model predictions for the equilibrium partial pressure of CO_2 over the loading of CO_2 in an aqueous solution of 5.46 M, 3 M and 2.3 M AMP for 313 K compared to the model predictions from Dash [31].



Figure 6-23. Model predictions for the equilibrium liquid phase concentration over the loading of CO₂ in an aqueous solution of 3.4 M AMP for 328 K compared to the model predictions from Dash [31].



Figure 6-24. Model predictions for the heat of absorption over the loading of CO_2 for an aqueous solution of 3.4 M AMP for 328 K compared to the model predictions from Dash [31].



Figure 6-25. Model predictions for the equilibrium partial pressure of AMP over the loading of CO₂ in an aqueous solution of 3.4 M AMP for different temperatures compared to the model results from Dash [31].

6.3.2.2 Aspen PlusTM example

In the following the Aspen $Plus^{TM}$ example for the AMP-H₂O-CO₂ solvent system is validated against experimental literature data.

In Figure 6-26, Figure 6-27, Figure 6-28, and Figure 6-29 the predictions for the equilibrium partial pressure of CO_2 for different concentrations and temperatures are compared to experimental data from literature (see Table 6-2).

Table 6-2. For validation used VLE data for the ternary system AMP-H₂O-CO₂.

[AMP] (mol/dm ³)	Temperature (K)	Source
2, 2.8, 3.4	303 - 323	Kundu
1.5, 3.4, 4.9	298 - 328	Dash
2, 3	293 - 353	Tontiwachwuthikul
2	313	Jane and Li
3.3	313 - 353	Seo and Hong

3.3	313 - 373	Li and Chang
3	313	Roberts and Mather
3	313	Yang

For a concentration of about 3 M AMP and temperatures from 313 K to 373 K the model predictions show good accordance to experimental data from Seo and Hong [68] and Li and Chang [69] (see Figure 6-26) as well as for experimental data from Jane and Li [70] for an aqueous solution of 2 M AMP and 313K (see Figure 6-27). The comparisons to experimental data from Tontiwachwuthikul [71], Dash [31] and Kundu [72] show significant deviations as depicted in Figure 6-27, Figure 6-28 and Figure 6-29, respectively.

The model predictions for the liquid phase concentration is compared to model predictions from Xu [73] and to ¹³C-NMR spectroscopy studies from Ciftja [74].

In Figure 6-34 the prediction for the heat of absorptions over the loading of CO_2 in an aqueous solution of 2.2 M AMP for 313 K is compared to experimental data from Kim [75]. The model prediction shows quite good accordance to the experimental data.

For the volatility of AMP for the system of $AMP-H_2O-CO_2$ not much data could be found in public literature. However, compared to the scarce experimental data from Nguyen [76] the model predictions show quite accurate results as can be seen in Figure 6-35.



Figure 6-26. Model predictions for the equilibrium partial pressure of CO_2 over the loading of CO_2 in an aqueous solution of 3.3 M AMP for 313 K, 333 K, 353 K and 373 K compared to exp. data from Seo and Hong [68] and Li and Chang [69].



Figure 6-27. Model predictions for the equilibrium partial pressure of CO₂ over the loading of CO₂ in an aqueous solution of 2.0 M AMP for 303 K, 313 K, 333 K and 353 K compared to exp. data from Tontiwachwuthikul [71], Kundu [72] and Jane and Li [70].



Figure 6-28. Model predictions for the equilibrium partial pressure of CO_2 over the loading of CO_2 in an aqueous solution of 3.4 M AMP for 298 K, 308 K, 318 K and 328 K compared to exp. data from Dash [31].



Figure 6-29. Model predictions for the equilibrium partial pressure of CO_2 over the loading of CO_2 in an aqueous solution of 3.4 M AMP for 303 K, 313 K and 323 K compared to exp. data from Kundu [72].



Figure 6-30. Model predictions for the equilibrium liquid phase concentration over the loading of CO₂ for an aqueous solution of 2.5 M AMP for 313 K compared to model predictions from Xu [73].



Figure 6-31. Model predictions for the equilibrium liquid phase concentration over the loading of CO₂ for an aqueous solution of 2.5 M AMP for 373 K compared to model predictions from Xu [73].



Figure 6-32. Model predictions for the equilibrium liquid phase concentration over the loading of CO₂ for an aqueous solution of 3.3 M AMP for 298 K compared to ¹³C-NMR spectroscopy studies from Ciftja [57].



Figure 6-33. Model predictions for the equilibrium liquid phase concentration over the loading of CO₂ for an aqueous solution of 3.3 M AMP for 308 K compared to ¹³C-NMR spectroscopy studies from Ciftja [57].



Figure 6-34. Model predictions for the heat of absorption over the loading of CO₂ in an aqueous solution of 2.2 M AMP for 313 K compared to exp. data of Kim 2013 [77].



Figure 6-35. Model predictions for the AMP volatility over the loading of CO_2 in an aqueous solution of 5.0 M AMP for 313 K and 333 K compared to exp. data from Nguyen [76].

6.3.3 Discussion and conclusion

The comparison of the model predictions, from the model with the reported parameters from Dash and his model prediction results for both sub-component systems shows, that the reproduction is not feasible only with the reported values from the publications. The validation results exposed strong deviations between the reproduced model and the model predictions from Dash. In a personal communication Dash explained, that in his publications some parameters such as the first parameters of the Henry's constants were adjusted by hand to fit the VLE data for the specific concentrations and temperatures and that an average value of those parameters is reported in the publications [78]. Therefore the Henry's constants were also changed by hand in the reproduced model, but unfortunately this does not help to fit the VLE data more accurately as can be seen in Appendix D. Due to this it is deduced, that also more parameters have been adjusted in Dash's work to fit the experimental data. Without knowledge of those adjustments, the accurate reproduction of those models is not possible. Moreover it would be worthwhile to obtain a model, which can predict the system behavior for different temperatures in a certain temperature range for a fixed concentration so that the model can be applied to the simulation of an absorption-desorption CO₂ capture process with varying temperature without changing the parameters. Another fact, that can be observed during the validation of the Aspen PlusTM example sub-component systems, is, that the model predictions from the validated models show strong deviations from Dash's VLE data, whereby they show quite good accordance with the other VLE data sources (compare Figure 6-9, Figure 6-10, Figure 6-11 and Figure 6-26, Figure 6-27, Figure 6-28). As the model shows just for the comparison with Dash's data such a big deviation, it can be concluded, that the experimental data from Dash deviates from the experimental data by the other sources, although they cannot be compared directly do to different concentrations and temperatures. Thus, the reliability of Dash's data has to be considered.

The validation of the Aspen $Plus^{TM}$ examples of the $PZ-H_2O-CO_2$ and $AMP-H_2O-CO_2$ in total shows quite accurate results for different sources of experimental data. The presented model results are predicted using the Aspen $Plus^{TM}$ examples without any parameter adjustments for the different temperatures and concentrations. By far

the largest deviation from experimental measurements can be observed for the prediction of the PZ volatility.

As the reproduction of Dash's models for the both sub-component systems is not possible and the Aspen $Plus^{TM}$ examples for AMP-H₂O-CO₂ and PZ-H₂O-CO₂ show quite accurate predictions apart from the PZ volatility, the Aspen $Plus^{TM}$ examples are chosen as subcomponent models for the quaternary solvent system AMP-PZ-H₂O-CO₂.

With respect to the application of the equilibrium model to a simple absorption process model (see Chapter 7) it would be expedient to obtain an accurate model within a certain concentration and temperature range. As described in Chapter 3.3.2 the AMP/PZ solvent system has already been tested in a pilot plant within the scope of the EU project CESAR. From this study pilot plant data for a solvent concentration of 28 w% AMP and 17 w% PZ (3.1 M AMP, 1.9 M PZ) is available. Thus it is favorably to have accurate sub-component models for a concentration of about 3 M AMP and 2 M PZ. As can be seen in the validation of the PZ Aspen PlusTM example model, the PZ model shows very good accuracy for an aqueous solution of 2 M PZ to the experimental data by Hilliard and Ermatchkov (see Figure 6-10). The AMP Aspen PlusTM example model shows quite good accordance for a 3 M concentration with experimental data from Seo and Hong and Li and Chang, but the accuracy could be improved by fitting the interaction parameters to those data.

6.4 Step 3: Parameter regression

As described in Chapter 6.2 the Aspen $Plus^{TM}$ examples for the $PZ-H_2O-CO_2$ and $AMP-H_2O-CO_2$ system are chosen as subcomponent models for the development of a model of the quaternary system $PZ-AMP-H_2O-CO_2$.

To improve the sub-component model for the ternary system AMP-H₂O-CO₂ with regards to a certain amine concentration as mentioned in Chapter 6.3.3, in the first step the electrolyte pair interaction parameters for this sub-component system are regressed to obtain a better fit to the selected VLE data. The regression results are presented and validated against the experimental VLE data. In the next step complementary interaction parameters for the overall quaternary system are selected

and tried to be regressed as well. However, problems occur within the regression, which are discussed.

6.4.1 Ternary system: AMP-H₂O-CO₂

As discussed in Chapter 6.3.3, in the first step, the ternary sub-component system $AMP-H_2O-CO_2$ is fitted to VLE data for an aqueous solution of about 3 M AMP to obtain a more accurate model for this concentration.

6.4.1.1 Data for regression

Four different data sources, which are summarized in Table 6-3, are found in literature for this concentration. The different data sets are compared in Figure 6-36.

Table 6-3. VLE data for the ternary system AMP-H₂O-CO₂ (~3 M AMP).

[AMP] (mol/dm ³)	Temperature (K)	Data points	Source
3.3	313 - 353	17	Seo and Hong [68]
3.3	313 - 373	28	Li and Chang [69]
3	313	10	Roberts and Mather [79]
3	313	8	Yang [80]



Figure 6-36. Comparison of VLE data from different sources for an aqueous solution of ~ 3 M AMP for 313 K.

As can be seen in the comparison, the four data sets show quite good accordance taking the deviation of the molarity into account. As can be seen in Table 6-3 the VLE data from Yang and Roberts and Mather are just available for one temperature. Data from Seo and Hong and Li and Chang are available for a temperature range from 313 K to 353 K and 313 K and 373 K, respectively. For regression the data set from Li and Chang is chosen, because it covers a bigger CO_2 loading range than the data set from Seo and Hong.

6.4.1.2 Regression results

Using the selected data set, the regression is done following the procedure described in Chapter 5.1.1. The regression results and their accuracy are reviewed in Table 6-4.

Table 6-4. Regression results for the regression of the

Parameter	C _{m,ca}	C _{ca,m}	D _{m,ca}	D _{ca,m}		
τ H2O-[AMPH ⁺ , HCO3 ⁻]	33.383	-24.447	-10000	8197.6		
Standard deviation	0,264 1,044 0,121 377,519					
Root mean square error (%)	0,451311008					

6.4.1.3 Model validation

Figure 6-37 shows the model predictions for the equilibrium partial pressure of CO_2 over the loading of CO_2 in an aqueous solution 3.3 M AMP for temperatures from 313 K to 373 K with the regressed pair parameters. It can be seen, that the model shows very good accuracy with the regressed interaction parameters. The predictions of the other properties such as speciation, heat of absorption and AMP volatility can be seen in the Appendix E.



Figure 6-37. Model predictions for the equilibrium partial pressure of CO₂ over the loading of CO₂ in an aqueous solution of 3.3 M AMP for 313 K, 333 K, 353 K and 373 K compared to experimental data from Yang [80].

6.4.2 Quaternary system: AMP-PZ-H₂O-CO₂

6.4.2.1 Physical properties

The physical properties for the components in the Aspen example of PZ-H₂O-CO₂ and AMP-H₂O-CO₂ are differing for some parameters, because the models have been developed at a different time and the Aspen PlusTM databases are actualized from time to time. Thus, for the deviating properties the newer ones are taken for the merged model. The physical properties, which are further used in the model of the quaternary system, are summarized in Table 6-5, Table 6-6 and Table 6-7.

Table 6-5. Coefficients for dielectric constants for H_2O , PZ and AMP.

Species	А	В		
H ₂ O	78.51	31989.38		
CO_2	1.449	0		
PZ	11.26958	8796		
AMP	21.9957	8451.2		

Components	H ₂ O	CO ₂	PZ	AMP	Ions
	(kPa)	(kPa)	(Pa)	(kPa)	
А	72.55	140.54	70.503	15.155	-1.00E+20
В	-7206.7	-4735	-7914.5	-3472.6	0
С	0	0	0	-107.32	0
D	0	0	0	0	0
E	-7.1385	-21.268	-6.6461	0	0
F	4.05E-06	0.040909	5.21E-18	0	0
G	2	1	6	0	0
			1		

Table 6-6. Antoine equation coefficients for molecular species and ions.

 Table 6-7. Coefficients of Henry's constant.

Components	CO ₂ -H ₂ O	CO ₂ -AMP	
C ₁	-145.316	19.52	
C_2	765.8882	-1205.2	
C ₃	32.24727	0	
C_4	-0.07395	0	

6.4.2.2 Interaction parameters

As describe in Chapter 5, the binary interaction parameters and the moleculeion interaction parameters from the sub-component systems are kept fixed for the quaternary systems. These parameters are summarized in Table 6-8 and Table 6-9. The interaction parameters from the AMP-H₂O-CO₂ system are replaced by the regressed parameters (see Chapter 6.4.1).

Parameter	a_{ij}	a_{ji}	b_{ij}	b_{ji}	α
H ₂ O-CO ₂	0	0	0	0	0.2
H ₂ O-AMP	-1.47633	7.086195	-29.7925	-1524.24	0.2
H ₂ O-PZ	0.510999	-0.9099	590.7102	-305.261	0.2

Table 6-8. Binary interaction NRTL parameters.

Table 6-9. Molecule-ion interaction pair parameters for elecNRTL model.

Parameter ⁵	C _{m,ca}	$C_{ca,m}$	D _{m,ca}	D _{ca,m}	α
τ H ₂ O-Ion	8	-4	0	0	0.2
$\tau \operatorname{CO}_2$ -Ion	8	-4	0	0	0.2
τ Amine-Ion	15	-8	0	0	0.2
τ H ₂ O-[AMPH ⁺ , HCO ₃ ⁻]	33.383	-24.447	-10000	8197.6	0.2
τ H ₂ O-[PZH ⁺ , HCO ₃ ⁻]	4.58244	-3.78863	0	0	0.2
τ H ₂ O-[PZH ⁺ , PZCOO ⁻]	10.3136	-5.39625	0	0	0.2

New complementary parameters (parameters, which include both, AMP and PZ species) are selected for regression based on their physical significance. One indicator for the physical significance is the speciation of the liquid phase. Components with a higher concentration are affecting the behavior of the solution more than components with a lower concentration. Thus, the accuracy of interaction parameters including these species is from more importance. Figure 6-38 shows the speciation of the PZ/AMP system predicted by Dash [30]. Although the reliability of Dash's data and model predictions has been discussed earlier in this report, his model predictions for speciation are chosen for assessing the physical significance of the species, because the most concentrated occurring components are always clearly assignable (see Chapter 6.3.1 and 6.3.2). As can be seen, the four most dominant species are AMP, AMPH⁺, HCO3⁻ and PZ.

 $^{^5}$ Parameter A_{ij} and A_{ji} refer in Aspen $Plus^{TM}$ to the parameter sheet GMELCC, parameter B_{ij} and B_{ji} to GMELCD and parameter α to GMELCN


Figure 6-38. Liquid phase concentration of an aqueous solution of 3.5 M AMP and 1.3 M PZ for a temperature of 318 K predicted by Dash [30].

Based on this speciation the molecule-ion interaction parameters listed in Table 6-10 are selected for regression.

Table 6-10. Selected molecule-ion interaction parameters for regression.

Molecule-ion interaction					
parameter					
τ H ₂ O-[AMPH ⁺ , PZCOO ⁻]					
τ H ₂ O-[AMPH ⁺ , PZ(COO ⁻) ₂]					
τ PZ-[AMPH ⁺ , HCO3 ⁻]					
τ AMP-[PZH ⁺ , HCO3 ⁻]					

6.4.2.2.1 Data for regression

In literature the VLE data for the quaternary system $PZ-AMP-H_2O-CO_2$ is very scarce. In Table 6-11 the available VLE data for different concentrations and temperatures is summarized.

[AMP]	[PZ]	W _{AMP}	W _{PZ}	Temperature	Course
(mol/dm^3)	(mol/dm^3)	(w-%)	(w-%)	(K)	Source
2	0.5	18.1	4.4	313 - 353	Yang [80]
2	1	18.1	8.7	313 - 353	Yang [80]
2	1.5	18.1	13.1	313 - 353	Yang [80]
3	0.5	27.1	4.4	313 - 353	Yang [80]
3	1	27.1	8.7	313 - 353	Yang [80]
3	1.5	27.1	13.1	313 - 353	Yang [80]
3	1.5	27.1	13.1	313 - 393	Brúder [81]
2.4	0.9	22	8	298 - 328	Dash [30]
2.8	0.6	25	5	298 - 328	Dash [30]
3.1	0.2	28	2	298 - 328	Dash [30]

Table 6-11. Available VLE data for the quaternary system PZ-AMP-H₂O-CO₂.

As discussed earlier in Chapter 6.3.3, the experimental VLE data from Dash for the sub-component systems did not show good accordance with experimental data from other authors. Thus, also the reliability of the VLE data for the quaternary system has to be questioned. Due to this reason and the fact, that the solvent concentration of Dash's data sets does not fit the desired concentration of about 3 M AMP and 2 M PZ, Dash's data is not considered for regression.

In Table 6-11 it can be seen, that there is no experimental VLE data available for a concentration of about 3 M AMP and 2 M PZ. The most representative available data set has a concentration of 3 M AMP and 1.5 M PZ. For this concentration data sets from two authors are available, Yang [80] and Brúder [82]. The data sets are compared in Figure 6-39.



Figure 6-39. Comparison of experimental VLE data from Brúder [82] and Yang [80] for an aqueous mixed solution of 3 M AMP and 1.5 M PZ for different temperatures.

The comparison of those data sets is difficult, because they cover different ranges of loading. Besides this there is no other reference available for assessing the reliability of those data sets. For a temperature of 313 K the data is in quite good accordance. With increasing temperature the data is deviating significantly from each other. Due to the significant differences not both data sets can be used for regression. Because the CO_2 loading range in the solvent during absorption is roughly between 0.1 and 0.6 mol CO_2 per mol AMP/PZ [83] the data set from Brúder is more useful. However, the quality of the data can't be stated.

6.4.2.2.2 Parameter regression

The regression is tried to be conducted as described in Chapter 5.1.1 and done for the AMP sub-component system. However, Aspen is not regressing the inserted experimental VLE data. When running the regression, Aspen PlusTM reports the regression as completed without any occurring warning or errors. However, the parameters are not regressed and remain as the initial values. Aspen PlusTM says, that this behavior can occur, when the parameters to be regress do not affect the used experimental data. But adjusting the selected parameters by hand shows clearly an effect on the VLE behavior of the system. As the regression already work very good for the AMP sub-component system, also a data regression for the PZ sub-component system is tried. But also for this system the regression does not work showing the same behavior than for the quaternary system. Based on this outcome it can be assumed, that this problem occurs due to the PZ system/components.

Because the problem could not be solved and no reason for this is known, the selected complementary interaction parameters are adjusted by hand to predict the VLE behavior in good accuracy to the selected experimental VLE data. As the for regression selected interaction parameter τ PZ-[AMPH⁺, HCO3⁻] does not show much effect on the VLE behavior, it is excluded from the parameter adjustment. In Table 6-12 the final adjusted parameters are summarized.

Table 6-12. Results of the adjusted molecule-electrolyte pair interaction parameters.

Parameter	C _{m,ca}	C _{ca,m}	D _{m,ca}	D _{ca,m}
τ H ₂ O-[AMPH ⁺ , PZCOO ⁻]	9	-5	0	0
τ H ₂ O-[AMPH ⁺ , PZ(COO ⁻) ₂]	7	-5	0	0
τ AMP-[PZH ⁺ , HCO3 ⁻]	12	-6.6	0	0

6.5 Step 4: Model validation

For the validation of the solvent properties of the resulting AMP-PZ-H₂O-CO₂ model no data is available besides the VLE data available for regression (see Table 6-11) and model predictions from Dash. As the reliability of Dash's data is uncertain, the model predictions are not used for validation. Figure 6-40 shows the comparison of the model predictions for the equilibrium partial pressure of CO₂ for different temperatures with the for regression selected VLE data from Brúder. The result is not perfect with respect to the selected VLE data, but shows very good accuracy in the mentioned CO₂ loading range of 0.1 to 0.6 mol CO₂ per mol AMP/PZ. Figure 6-41, Figure 6-42 and Figure 6-43 show the model predictions for the speciation, heat of absorption and amine volatility, respectively.



Figure 6-40. Model predictions for the equilibrium partial pressure of CO₂ over the loading of CO₂ in an aqueous solution of 3 M AMP and 1 M PZ for 313 K, 333 K and 353 K compared to experimental data from Brúder [82].



Figure 6-41. Model predictions for the equilibrium liquid phase concentration over the loading of CO₂ in an aqueous solution of 3 M AMP and 1.5 M PZ for 333 K.



Figure 6-42. Model predictions for the heat of absorption over the loading of CO_2 in an aqueous solution of 3 M AMP and 1.5 M PZ for 313 K, 333 K and 353 K.



Figure 6-43. Model predictions for the AMP and PZ volatility over the loading of CO_2 in an aqueous solution of 3 M AMP and 1.5 M PZ for 313 K, 333 K, 353 K, 373 K and 393 K.

7 Absorption process modeling

For further validation of the modeled solvent system an absorption process is modeled with an equilibrium based RadFrac column. The flowsheet is shown in Figure 7-1. The lean solvent is fed into the column top and absorbs the CO_2 from the incoming flue gas. The composition of the incoming flue gas is summarized in Table 7-1. The treated gas is released at the top of the column and the CO_2 rich solvent leaves the absorber at the bottom.



Figure 7-1. Absorption process flowsheet.

Mass flow	m ³ /h	5000
Pressure	bar	1.15
Temperature	°C	40
Composition		
N_2	mol-%	0.81
CO_2	mol-%	0.13
H ₂ O	mol-%	0.05
O ₂	mol-%	0.01

Table 7-1. Flue gas flow rate and composition.

7.1 Absorber optimization

The absorber is modeled following the method described in Alie et al. [84]. To reach a targeted CO₂ recovery of 90 % a certain lean solvent flow has to be provided for absorption. For this, a design spec is defined, which calculates the amount of recovered CO₂ and determines the required lean solvent flow rate. The flow rate depends on the amine concentration in the solvent solution, the required CO₂ removal and the difference between the CO₂ loading of lean and rich solvent solution $(\alpha_{rich} - \alpha_{lean})$. The solvent circulation rate can be expressed as follows:

$$\dot{m}_{solvent} = \frac{\dot{m}_{fg} x_{CO_2} \varepsilon}{(\alpha_{rich} - \alpha_{lean}) \cdot [AMP + PZ]}$$
7-1

Where,

 \dot{m}_{fg} is the flue gas flow rate in mol per second, x_{CO_2} is the mole fraction of CO₂ in the flue gas, ε is the fraction of total CO₂ absorbed from the flue gas, and, $(\alpha_{rich} - \alpha_{lean}) \cdot [AMP + PZ]$ is the cyclic CO₂ capacity.

Theoretically, the minimum lean solvent flow rate would be achieved with an infinite number of stages. As the performance benefit from the addition of extra trays diminish with an increase in the number of stages, an criterion from Alie [84] is adopted to select the minimum amount of stages N_{min} . It is defined as the number of stages at which the percent difference in lean solvent flow rate was less than or equal to 0.5 % from the run with N-2 stages. This is done for lean solvent CO₂ loadings from 0 to 0.4 mol CO₂ per mol AMP/PZ. The results are shown in Figure 7-2. The data points in the figure represent the determined minimum amount of stages. For a lean solvent CO₂ loading of 0.2 N_{min} is 19 and cannot be seen in the figure. The criterion for the determination of N_{min} appears to be quite strict, as the lean solvent flow rate already reaches relatively constant values at lower numbers of stages. Thus, a number of 12 stages is set as an average value for N_{min} .



Figure 7-2. Required lean solvent flow rate as a function of the number of stages.

For an equilibrium column with 12 stages the CO_2 loading profiles and temperature profiles over the absorber are shown for lean solvent CO₂ loadings from 0 to 0.4 mol CO₂ per mol AMP-PZ in Figure 7-3 and Figure 7-4, respectively. In Figure 7-5 the absorber bottom stage conditions for the different lean loadings are compared to flash predictions for the CO_2 equilibrium partial pressure for the bottom stage temperatures. It can be noted, that the variation of the lean solvent loading has a strong impact on the CO_2 loading and temperature profiles over the absorber. A large difference in the outgoing rich solvents loading can be observed. It varies from about 0.78 mol CO₂ per mol AMP-PZ for a lean loading of 0 to 0.2 mol CO₂ per mol AMP-PZ to about 0.62 mol CO₂ per mol AMP-PZ for a lean loading of 0.3 to 0.4 mol CO₂ per mol AMP-PZ. The temperature profiles reach high values up to 70 °C for a lean loading of 0.2 to 0.3 mol CO₂ per mol AMP-PZ and remain very high in the bottom stage for lean loading of 0.3 and 0.4 mol CO₂ per mol AMP-PZ. Relating the temperature profile to the concentration profile, the decrease in rich loading is reasonable due to the higher temperature in the bottom stage. The different development of the temperatures for the different lean solvent loadings could be related to differing heats of absorption for different CO₂ loadings in the solvent (see Figure 6-42). However, this high temperatures are not common for the case of CO_2 absorption with amine solvents [85].



Figure 7-3. CO₂ loading profile in the column for lean solvent CO₂ loadings between 0.0 to 0.4 mol CO₂ per mol AMP-PZ.



Figure 7-4. Temperature profile over the absorber for lean solvent CO₂ loadings between 0.0 to 0.4 mol CO₂ per mol AMP-PZ.



Figure 7-5. Flash predictions for bottom stage temperatures compared to bottom stage conditions for lean solvent CO₂ loadings between 0.0 to 0.4 mol CO₂ per mol AMP-PZ.

For a kinetic based absorption-desorption process model of the AMP-PZ solvent system (with comparable process conditions: 90% CO₂ removal, same flue gas flow and CO₂ concentration, see Table 7-1) Kvamsdal et al. reported an predicted rich solvent CO₂ loading of 0.559 mol CO₂ per mol AMP-PZ for an incoming lean solvent flow of 12.5 m³/h with a loading of 0.128 mol CO₂ per mol AMP-PZ [44]. For this lean solvent loading the equilibrium based absorber model predicts a rich solvent loading of about 0.78 mol CO₂ per mol AMP-PZ in an optimized lean solvent flow rate of 9.04 m³/h. It can be noted, that in the equilibrium based absorber model a higher rich solvent CO₂ loading is reached, which results in a lower lean solvent flow rate required for the removal of the same amount of CO₂, compared to the kinetic model by [44]. Form the deviation of the cyclic capacity, on the one hand, could be concluded, that the reliability of the model is not good. On the other hand, this could indicate, that the kinetic behavior of the system may restricts the cyclic capacity compared to the equilibrium behavior. For a further investigation of this reasoning, kinetics would need to be added to the model.

7.2 Conclusion

The reliability of the absorber model cannot be assessed, because no data for validation is available. However, the high temperature profiles in the absorber and the significantly difference in the reached rich solvent loadings for the different incoming lean solvent loadings as well as the comparison to a kinetic based study let assume, that the equilibrium model (developed in Chapter 6) has need for further improvement. To make a comparison to the available kinetic models and pilot plant data possible, kinetics would need to be added to the model.

8 Conclusions and recommendations

8.1 Conclusions on implementation of novel carbon capture solvents in Aspen PlusTM

In the introduction of this study three research questions were formulated. This chapter will conclude on this study by answering the research questions and drawing conclusions on the used research methodology.

 Which novel post-combustion carbon capture solvent is suitable as case study for the implementation in Aspen PlusTM ?

For the selection of a solvent system for PCC the availability of reliable thermodynamic data, describing the physical and chemical properties of each compound and the thermodynamic interactions of the participating species, is required. It has been found, that the estimation of missing physical properties with group contribution methods does not deliver sufficient results for the case of taurine. It is not certain if this is also the case for other electrolyte solvent molecules and would need to be answered. Besides this, these estimation methods cannot be applied to ions for the estimation of physical properties. Thus, the availability of the parameters in the Aspen PlusTM, NIST or DECHEMA databases or the experimental data needed for the regression of those parameters is a key requirement for the selection of a solvent. Based on this requirement, a piperazine activated aqueous solution of 2-amino-2methyl-1-propanol was selected. For this novel solvent system the physical properties for all participating species and interaction parameters for the subcomponent systems are available in the Aspen PlusTM database and Aspen PlusTM examples. Additionally, experimental data for the regression of the required complementary parameters was found.

• What are the data requirements for the thermodynamic modeling of PCC solvents?

The data requirements were concluded based on the theory behind the eNRTL model. A large amount of parameters for the participating molecules, molecular

solutes and ions are required, including standard data but also somewhat exotic data as established in Chapter 4. To increase the use of process simulation tools for the investigation of novel solvents for PCC, the available data would need to be extended for these solvents. This can be done by extending public databases or extending your own database by doing laboratory measurements. However, this would require extensive effort.

Due to the high requirements for the modeling in Aspen $Plus^{TM}$ in further investigation it should be discussed, whether the use of other simulation tools with less data requirements, may give a better tradeoff between effort and results for the modeling of PCC solvents compared to Aspen $Plus^{TM}$.

• How can experimental data be included in the modeling tool to obtain the required correlations/parameters?

For the conversion of experimental data to the required correlations/parameters the Data Regression System (DRS) in Aspen PlusTM can be used. It has been found, that with this tool the whole range of required parameters can be regressed, if suitable experimental data is available. However, due to the high data availability for the selected solvent system, this study focused only on the regression of molecule-ion interaction parameters. A modeling procedure was developed, from which it can be concluded that the regression of the interaction parameters cannot be done independently, as they are highly correlated. Thus, the regression has to follow a certain order as was established in Chapter 5. It was found that the reported VLE data for CO₂ absorption solvent systems cannot directly be inserted to the given data sets in Aspen PlusTM. For this, a solution has been found, which is described in Chapter 5.1.1. The regression of interaction parameters was done for two different solvent systems, the sub-component system AMP-H₂O-CO₂ and the complete solvent system AMP-PZ-H₂O-CO₂. For the former, the regression worked and delivered accurate results, for the latter, the DRS did not converge on any coefficient values, whereby no error or warning was reported from Aspen PlusTM. Those problems could not be related to any thermodynamic reasons in this study (see Chapter 6.4.3). Further research should elaborate, whether the problems were related to PZ or may represent a bug in Aspen PlusTM.

Besides conclusions related to the research questions, some additional lessons can be drawn. Although experimental VLE data for regression was found from a number of different sources, it was difficult to assess their quality. The data deviated from each other and made it difficult to choose a source for regression. Particularly because it was not always reported how the data was gathered and which measurement method is the most reliable one. A similar problem occured to the data for validation. For some properties (e.g. heat of absorption or amine volatility) there was very little or even no data available and it was not known how reliable it was. In order to build a highly accurate reliable model, the required experimental data should be obtained by in-house experiments, if possible, or through a collaboration with a lab to ensure the quality of the data.

Additionally it was found, that the Aspen PlusTM examples (at least the ones used in this work) are not from high detail, as only a very little number of moleculeion interaction parameters were selected for modeling the system. Thus, they do not deliver highly accurate predictions, especially for systems with a high number of participating species and reactions like PZ-H₂O-CO₂. Hence, it is concluded, that Aspen PlusTM example models deliver good estimates for fast assessments, but do not replace highly accurate models.

Taking a look at the theory behind the eNRTL model indicates that it is a very complex topic and requires a high grade of knowledge and skills to understand the thermodynamics and all interdependencies of the sub-models and their effect on the parameters. During this study, many different sources were considered to develop the modeling procedure and find information and support in the field of interaction parameter regression. Besides reviewing literature studies, the Aspen PlusTM support desk, authors from related publications and known experts were contacted. It turned out, that there are only few people dealing with this topic and have the required experience. The most reliable support was found at the Mcketta Department of Chemical Engineering at The University of Texas, Austin.

8.2 Discussion on the thesis process

When I was choosing this master thesis topic, I was not aware of the depth and complexity of the theory behind the eNRTL and related models in Aspen PlusTM. But I liked the idea to gain further knowledge about carbon capture solvents and to improve my skills in the use of Aspen PlusTM. After first research it quickly turned out that the research goal was quite ambitious for the given time frame of 5 month starting from a point without founded knowledge about the thermodynamics behind the eNRTL model and all interdependencies of the sub-models and their effect on the parameters. High efforts were focused on finding support in modeling electrolyte systems, as only little support within this field could be found in the closer research environment. Moreover, it turned out, that there are only few people dealing with this topic and have the required experience as already mentioned above. Therefore, next time starting a highly specialized study, I would ensure having access to support in the required field in forehand.

The research process was developing during the study. It took some time to figure out the data requirements, knowledge of the present models and their interactions. Especially during the reproduction of Dashs models trial and error methods were applied to investigate the interactions of the used parameters in sense of 'learning by doing'. After gaining more knowledge, the research process became more structured and a more detailed planning was done for the further research such as validation of subcomponent systems and regression of complementary parameters. Looking back, it would have been more effective to put more effort on gaining the whole knowledge about the theory behind the topic before starting modeling in Aspen PlusTM. However, this approach made it more interactive.

Retrospectively, I would say this study combined two goals. On the one hand, developing a modeling procedure for amine solvent using the eNRTL model in Aspen PlusTM, on the other hand, building an accurate model of a novel PCC solvent. Depending on the goal, I would follow a revised approach based on the gained experience in this study. For describing a general modeling procedure, a well known solvent should have been selected to avoid problems with data reliability and ensure a good validation and high detail of the developed modeling procedure. Building up on

this procedure, a novel solvent can be selected. Hereby it should be first focused on obtaining experimental data with good quality. In this study, those two goals were followed parallel, which lead to lacking information and restrictions of the scope of the research.

From this this research I gain insights which I am going to incorporate in further projects:

- ensure support before starting a highly specialized study;
- try to build up a more detailed framework in the beginning of a study;
- revise research planning frequently depending on the process and outcome of the ongoing work;
- be even more critical with the quality of research publications;
- have valuable research results does not always mean having good and expected results and conclusions.

8.3 Recommendations for future research

Summarizing the developed modeling procedure for amine solvents in Aspen PlusTM and the gained experience during the parameter regression helps to understand the modeling and promotes the use of process simulation tools for the investigation of PCC solvents. However, it also made evident the need for further research and investigation. To obtain an even better understanding of the thermodynamic modeling of novel PCC solvents in Aspen PlusTM additional work the following is recommended:

- As the data conversion mainly focused on the regression of molecule-ion interaction parameters, further work should focus on the conversion of data to obtain physical properties and binary interaction parameters.
- It should be focused on the reliability and detail of the used data. In order to build up an highly accurate model it is recommended to obtain the required experimental

data by in-house experiments or by collaboration with a lab to ensure good data quality.

- If the regression problems related to PZ containing systems cannot be solved, maybe an external regression of the interaction parameters should be considered, as no thermodynamic founded reason could be related to these problems.
- It should be discussed and assessed whether the use of other simulation tools with less data requirements, may give a better tradeoff between effort and results for the modeling of PCC solvents compared to Aspen PlusTM.

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Appendix A: Solvent Selection

 Table A - 1. Methods, which can be applied for the estimation of certain pure component physical properties, and their information requirements.

Description	Parameter	Method	Information Required
Molecular weight	MW	FORMULA	Structure
Normal boiling point	ТВ	JOBACK	Structure
		OGATA-TSUCHIDA	Structure
		GANI	Structure
		MANI	TC, PC,
			Vapor pressure data
Critical temperature	ТС	JOBACK	Structure, TB
		LYDERSEB	Structure, TB
		FEDORS	Structure
		AMBRODE	Structure, TB
		SIMPLE	MW, TB
		GANI	Structure
		MANI	Vapor pressure data
Critical pressure	PC	JOBACK	Structure
		LYDERSEN	Structure, MW
		AMBROSE	Structure, MW
		GANI	Structure
Critical volume	VC	JOBACK	Structure
		LYDERSEN	Structure
		AMBROSE	Structure
		RIEDEL	TB, TC, PC
		FEDORS	Structure
		GANI	Structure
Critical compressibility factor	ZC	DEFINITION	TC, PC, VC
Standard heat of formation	DHFORM	BENSON	Structure
		JOBACK	Structure
		BENSONR8	Structure
		GANI	Structure
Standard Gibbs free energy of	DGFORM	JOBACK	Structure

formation		BENSON	Structure
		GANI	Structure
Acentric factor	OMEGA	DEFINITION	TC, PC, PL
		LEE-KESLER	TB, TC, PC
Solubility parameter	DELTA	DEFINITION	TB, TC, DHVL, VL
UNIQUAC R	UNIQUAC R	BONDI	Structure
UNIQUAC Q	UNIQUAC Q	BONDI	Structure
Parachor	PARC	PARACHOR	Structure
Solid enthalpy of formation at	DHSFRM	MOSTAFA	Structure
25C			
Solid Gibbs energy of formation	DGSFRM	MOSTAFA	Structure
at 25C			
Aqueous infinite dilution Gibbs	DGAQHG	AQU-DATA	DGAQFM
energy of formation for the		THERMO	DGAQFM, S025C
Helgeson model		AQU-EST1	DGAQFM
		AQU-EST2	S025C
Aqueous infinite dilution	DHAQHG	AQU-DATA	DGAQFM
enthalpy of formation for the		THERMO	DGAQFM, S025C
Helgeson model		AQU-EST1	DGAQFM
		AQU-EST2	S025C
Entropy at 298.15 K for the	S25HG	AQU-DATA	S025C
Helgeson model		THERMO	DGAQFM, DHAQFM
		AQU-EST1	DGAQFM
		AQU-EST2	DHAQFM
Helgeson OMEGA heat	OMEGHG	HELGESON	S25HG, CHARGE
capacity coefficient			
Ideal gas heat capacity	CPIG	DATA	Ideal gas heat capacity
			data
		BENSON	Structure
		JOBACK	Structure
		BENSONR8	Structure
Vapor pressure	PL	DATA	Vapor pressure data
		RIEDEL	TC, PC, PL
		LI-MA	MW, TB
		MANI	TC, PC, vapor pressure
			data
Enthalpy of vaporization	DHVL	DATA	Heat of vaporization

			data
		DEEINITION	
		DEFINITION	IC, PC, PL
		VETERE	MW, TB
		GANI	Structure
		DUCROS	Structure
		LI-MA	Structure, TB
Liquid molar volume	VL	DATA	Liquid molar volume
			data
		GUNN-YAMADA	TC, PC, OMEGA
		LEBAS	Strucutre
Liquid viscosity	MUL	DATA	Liquid viscosity data
		ORRICK	Structure, MW, VL, TC,
			PC
		LETSOU-STIEL	MW, TC, PC, OMEGA
Vapor viscosity	MUV	DATA	Vapor viscosity data
		REICHENBERG	Structure, MW, TC, PC
	KL	DATA	Liquid thermal
			conductivity data
		SATO-RIEDEL	MW, TB, TC
Vapor thermal conductivity	KV	DATA	Vapor thermal
			conductivity data
Surface tension	SIGMA	DATA	Surface tension data
		BOCK-BIRD	TB, TC, PC
		MCLEOD-SUGDEN	TB, TC, PC, VL, PARC
Solid heat capacity	CPS	DATA	Solid heat capacity data
			Structure
		MOSTAFA	
Helgeson C heat capacity	CHGPAR	HG-AQU	OMEGHG, CPAQ0
coefficient		HG-CRIS	OMEGHG, S25HG,
			CHARGE
		HG-EST	IONTYP, OMEGHG,
			S25HG
Liquid heat capacity	CPL	DATA	Liquid heat capacity
			data
		RUZICKA	Structure
		1	

Acronym	Name	Type*	Structure	Data availability	Reference
		ALKA	NOLAMINES		
1-(2HE) PRLD	1-(2- hydroxyethyl) pyrrolidine	3-с	ОН	low	[86, 87]
1-2(HE) PP	1-(2- hydroxyethyl) piperidine	3-c	Слудон	low	[86, 87]
1M-2PPE	1-methyl-2- piperidineethanol	3-с	ОН	low	[86, 87]
2-PE	2- piperidineethanol	2-ch	OH NH	low	[37]
2-PM	2- piperidinemethan ol	2-ch	ОН	low	[37]
AEPD	2-amino-2-ethyl- 1,3-propanediol	1-h	но Он NH2	low	[37, 88]
AHPD	2-amino-2- hydroxymethyl- 1,3-propanediol	1-h	HO HO OH	low	[37]
AMP	2-amino-2- methyl-1- propanol	1-h		high	[26, 37, 44, 81-83, 88-93]
AMPA	2-amino-2- methylpropionic acid	1-h		low	[37]

Table A - 2. List of solvents for	post-combustion CO ₂ capture.
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AMPD	2-amino-2- methyl-1,3- propanediol	1-h	но ОН NH2	low	[37, 94]
APPA	2-amino-2- phenylpropionic acid	1-h	H ₂ N OH	low	[37]
DEA	diethanolamine	2	HO	high	**
DEA-1,2- PD	3-diethylamino- 1,2-propanediol	3	∕_N∕_C ↓ OH	low	[86, 87]
DEA-1P	3-diethylamino-1- propanol	3	~~~~o	low	[86, 87]
DEEA	diethylethanolami ne	3	он	medium	[86, 87, 95]
DGA	diglycolamine	1	H ₂ N	high	**
DIPA	diisopropylamine	2-h		high	**
DMA-2P	1-dimethylamino- 2-propanol	3	OH I	low	[86, 87]
DMEA	dimethylethanola mine	3	∼ _N ∕∕OH I	medium	[88, 96, 97]
EDA	ethylenediamine	1/1	$H_2N^{NH_2}$	high	[90-93, 98, 99]
HEP	hydroxyethyl piperazine	2/3-с		low	[88]
MAPA	3-(methylamino) propylamine	1/2	N H NH ₂	medium	[96, 97]
MDA	1,8-p-menthane diamine	1/1-h	H ₂ N NH ₂	low	[37]

MDEA	N- methyldiethanol- amine	3	но Лилон	high	**
MEA	mono- ethanolamine	1	HONH2	high	**
РА	pipecolinic acid	2-ch	С ОН	low	[37]
PZ	piperazine	2/2-c		high	[26, 44, 81-83, 88, 89, 91-93]
TBA	tert-butylamine	1-h	\rightarrow ^{NH₂}	low	[37]
TBAE	2-(tert- butylamino) ethanol	2-h	→ N → OH	low	[37]
TEA	triethanolamine	3	но Лон	high	**
		AMI	INO ACIDS		
alanine	_	α-AS	O NH ₂ OH	low	[100-102]
glycine	-	AS	H ₂ N, OH	low	[100, 101, 103]
glycine proline	-	AS α-AS		low low	[100, 101, 103] [100-102]
glycine proline sarcosine	-	AS α-AS α-AS		low low medium	[100, 101, 103] [100-102] [33, 100- 102, 104, 105]

*primary: 1, secondary: 2, tertiary: 3, cyclic: c, sterically hindered: h, polyamine: e.g. 1/2 ** no references are reviewed for the solvents, which are implemented in Aspen already (excluding AMP, PZ)

Table A - 3. List of examples for studied amine blends as solvents for post-combustionCO2 capture.

System	Data availability	Reference
AMP-PZ	high	[26-32]
DEA-MDEA	high	Aspen Plus TM example
MEA-MDEA	high	Aspen Plus TM example
PZ-MDEA	high	Aspen Plus TM example
PZ-MEA	high	Aspen Plus TM example
Sulfolane-DIPA	high	Aspen Plus TM example
Sulfolane-MDEA	high	Aspen Plus TM example

Table A - 4. Estimated temperature-dependent parameters for taurine.

Parameter	Unit	Value	Method
CPIG-1	K, J/kmol K	46092	JOBACK
CPIG-2	K, J/kmol K	323.29	
CPIG-3	K, J/kmol K	-0.0932	
CPIG-4	K, J/kmol K	-2.98000	
CPIG-5	K, J/kmol K	0	
CPIG-6	K, J/kmol K	0	
CPIG-7	K, J/kmol K	280	
CPIG-8	K, J/kmol K	1100	
CPIG-9	K, J/kmol K	36029.2	
CPIG-10	K, J/kmol K	19.7689	
CPIG-11	K, J/kmol K	1.5	

PLXANT-1	K, Pa	52.772	RIEDEL
PLXANT-2	K, Pa	-7201.42	(TC, PC, PL)
PLXANT-3	K, Pa	0	
PLXANT-4	K, Pa	0	
PLXANT-5	K, Pa	-4.16631	
PLXANT-6	K, Pa	1.37855e-18	
PLXANT-7	K, Pa	6	
PLXANT-8	K, Pa	457.65	
PLXANT-9	K, Pa	759	
DHVLWT-1	K, J/kmol	42929100	DEFINITION
DHVLWT-2	K, J/kmol	457.65	
DHVLWT-3	K, J/kmol	0.440138	
DHVLWT-4	K, J/kmol	-0.162495	
DHVLWT-5	K, J/kmol	457.65	
MULAND-1	K, Pa s	71.2611	LETSOU-STIEL
MULAND-2	K, Pa s	-4674.18	(MW, TC, PC,
MULAND-3	K, Pa s	-11.2164	OMEGA)
MULAND-4	K, Pa s	457.65	
MULAND-5	K, Pa s	751.41	
KLDIP-1	K, Watt/m K	-0.602111	SATO-RIEDEL
KLDIP-2	K, Watt/m K	0.0054013	(MW, TB, TC)
KLDIP-3	K, Watt/m K	-1.48945e-05	
KLDIP-4	K, Watt/m K	1.76935e-08	
KLDIP-5	K, Watt/m K	-7,92096232E-12	
KLDIP-6	K, Watt/m K	457,65	
KLDIP-7	K, Watt/m K	751,41	
SIGDIP-1	K, N/m	0,108673404	BOCK-BIRD
SIGDIP-2	K, N/m	1,22222222	(TB, TC, PC)
SIGDIP-3	K, N/m	6,00078488E-10	
SIGDIP-4	K, N/m	-6,61320765E-10	
SIGDIP-5	K, N/m	2,67115061E-10	

SIGDIP-6	K, N/m	457,65
SIGDIP-7	K, N/m	743.82

Appendix B: Aspen PlusTM nomenclature

Aspen PlusTM Scalar Parameter Nomenclature

API	Standard API gravity
CHARGE	Ionic Charge number (positive for cations, negative for anions)
CHI	Stiel polar factor
DGAQFM	Aqueous phase free energy of formation at infinite dilution and 25 deg C For ionic species and molecular solutes in electrolyte systems
DGAQHG	Helgeson infinite dilution Gibbs energy of formation
DGFORM	Standard free energy of formation for ideal gas at 25 deg C
DGFVK	Parameter for the Gibbs free energy of formation. Used by the van Krevelen models
DGSFRM	Solid free energy of formation at 25 deg C
DHAQFM	Aqueous phase heat of formation at infinite dilution and 25 deg C. For ionic species and molecular splutes in electrolyte systems
DHAQHG	Helgeson infinite dilution enthalpy of formation
DHFORM	Standard enthalpy of formation for ideal gas at 25 deg C
DHFVK	Parameter for the enthalpy of formation. Used by the van Krevelen models
DHSFRM	Solid enthalpy of formation at 25 deg C
DHVLB	Enthalpy of vaporization at TB
DLWC	Vector indication diffusing or non-diffusing components for Wilke- Chang Model. Enter 1 for diffusing component or 0 or non-diffusing component.
DVBLNC	Vector indication diffusing or non-diffusing components for Chapman-
	Enskog-Wike-Lee Model. Enter 1 for diffusing component or 0 or nondiffusing
	component
HCOM	Standard enthalpy of combustion at 298.2 K
IONRDL	Riedel ionic coefficient for correction to the liquid mixture thermal conductivity of a mixture due to the presence of electrolytes
IONTYP	Ion type for the Criss-Cobble aqueous infinite dilution ionic heat
	capacity equation (1=cations; 2=simple anions, OH-; 3=oxy anions; 4=acid oxy anions; 5=H+)
MUP	Dipole moment
MW	Molecular weight
OMEGA	Pitzer acentric factor
OMEGHG	Helgeson Omega heat capacity coefficient
PC	Critical Pressure
RADIUS	Born radius of ionic species
RHOM	Mass density
RKTZRA S25HG	Parameter for the Rackett liquid molar volume model Helgeson entropy at 25 deg C

Absolute entropy at 25 deg C used in the Criss-Cobble equation for estimation of aqueous infinite dilution ionic heat capacity
Sum of element entropies at 25 deg C
Standard specific gravity at 60 deg F
Normal boiling point
Critical temperature
Freezing point temperature
Reference temperature when solid reference state is used ($RSTATE = 3$).
TREFHS is used together with DHSFRM and DGSFRM
Liquid molar volume at TB
Critical volume
Critical volume for the Rackett liquid model; defaults to VC
Standard liquid volume at 60 deg F
Critical compressibility factor

Aspen PlusTM Temperature Dependent Nomenclature

AHGPAR	Helgeson Equation of state coefficients (for ions in the chemical reactions)
ATOMNO	Vector containing the atom types (atomic numbers) for a given molecule (e.g., H=1, C=6, O=8). Must use the vector NOATOM to define the number of occurrences of each atom.
CHGPAR	Helgeson C Heat Capacity coefficient (for ions in the chemical reactions)
CPAQ0	Aqueous phase heat capacity at infinite dilution polynomial. If no values are given then uses Criss-Cobble equation to calculate heat capacity.
CPDIEC	Pure component dielectric constant coefficients of nonaqueous solvents
CPIG	Ideal gas heat capacity
CPIGDP	DIPPR ideal gas heat capacity equation is used for most pure components
CPLXP1	Barin liquid phase heat capacity for the first temperature range
CPLXP2	Barin liquid phase heat capacity for the second temperature range
CPSDIP	Coefficients for the DIPPR solid heat capacity equation
CPSPO1	Solids heat capacity polynomial
DHVLDP	Pure component heat of vaporization coefficients for the DIPPR heat of vaporization equation
DHVLWT	Watson Heat of Vaporization equation for pure components
DNLDIP	DIPPR liquid density equation for pure components if DNLDIP is available (pure component liquid molar volume)
DNSDIP	DIPPR solid density equation
IONMOB	Coefficients for the Jones-Dole correction to liquid mixture viscosity due to the presence of electrolytes (moles)
IONMUB	Coefficients for the Jones-Dole correction to liquid mixture viscosity due to the presence of electrolytes (volume/mole)
KLDIP	Pure component liquid thermal conductivity coefficients for the DIPPR liquid thermal conductivity equation
KSPOLY	Solid Thermal conductivity
--------	--
KVDIP	Pure component vapor thermal conductivity for low pressure gasses coefficients for the DIPPR vapor thermal conductivity equation
MULAND	Pure component liquid viscosity coefficients for the Andrade Liquid Viscosity equation
MULDIP	Pure component liquid viscosity coefficients for the DIPPR Liquid Viscosity equation
MUVDIP	Pure component low pressure vapor viscosity coefficients for the DIPPR Liquid Viscosity equation
NOATOM	Vector containing the number of each type of element in the component. Must be used with ATOMNO.
PCES	Parameters Estimation by the Aspen Physical Property System
PLXANT	Coefficients for the Extended Antoine vapor pressure equation for a liquid
PSANT	Pure component Coefficients for Solid Antoine vapor pressure equation
SIGDIP	Pure component liquid surface tension coefficients for the DIPPR liquid surface tension equation
VLBROC	Brelvi-O-Connell Volume Parameter
VLPO	IK-CAPE liquid density equation for pure components if VLPO is available (pure component liquid molar volume)
VSPOLY	Pure component coefficients for the solid molar volume equation
WATSOL	Coefficients for the water solubility equation model that calculates solubility of water in a hydrocarbon-rich liquid phase. This model is used automatically when you model a hydrocarbon-water system with free- water option

Appendix C: Physical properties and interaction parameters

Table C - 1. Coefficients for dielectric constants for H₂O and PZ reported by Dash [29].

Species	А	В
H ₂ O	78.65	31989
PZ	4.253	1532.2

 Table C - 2. Antoine equation coefficients for molecular species and ions reported by

 Dash [29].

Components	H ₂ O	CO ₂	PZ	Ions
А	72.55	140.54	70.503	-1.00E+20
В	-7206.7	-4735	-7914.5	0
С	0	0	0	0
D	0	0	0	0
Ε	-7.1385	-21.268	-6.6461	0
F	4.046E-06	0.040909	5.2106E-18	0
G	2	1	6	0

Table C - 3. Coefficients of Henry's constant reported by Dash [29].

Components	CO ₂ -(H ₂ O-PZ)
C_1	164.63
C_2	-8477.7
C ₃	-21.95743
C_4	0.005781

Table C - 4. Binary interaction NRTL parameters reported by Dash [29].

Parameter	a _{ij}	a _{ji}	b _{ij}	b _{ji}
H ₂ O-PZ	1.321	6.996	684.9	-2932.1
$H_2O-H^+PZCOO^-$	7.933	-4.033	0.0	0.0

Table C - 5. Molecule-ion interaction pair parameters for elecNRTL model reported byDash [29].

Parameter ⁶	C _{m,ca}	C _{ca,m}	D _{m,ca}	D _{ca,m}	α
τ H ₂ O-[PZH ⁺ , HCO ₃ ⁻]	8.9247	-4.032	0	0	0.2
τ H ₂ O-[PZH ⁺ , PZ(COO ⁻) ₂]	7.9342	-4.032	0	0	0.2
τ H ₂ O-[PZH ⁺ , PZCOO ⁻]	7.9349	-4.032	0	0	0.2
τ PZ-[PZH ⁺ , HCO ₃ ⁻]	9.9160	-2.016	0	0	0.2
τ PZ-[PZH ⁺ , PZCOO ⁻]	9.9165	-2.016	0	0	0.2
τ PZ-[PZH ⁺ , PZ(COO ⁻) ₂]	7.9342	-4.032	0	0	0.2
τ PZ-[H3O ⁺ , HCO ₃ ⁻]	9.9165	-2.016	0	0	0.2
τ PZ-[H3O ⁺ , PZ(COO ⁻) ₂]	9.9165	-2.016	0	0	0.2

 Table C - 6. Coefficients for the equilibrium constants for elecNRTL model reported by

 Dash [29].

Coefficient	А	В	С	D	T(K)
K ₁	132.899	-13445.9	-22.477	0	273-498
K_2	231.465	-12092.1	-36.782	0	273-498
K ₃	216.049	-12431.7	-35.482	0	273-498
K_4	514.314	-34910.9	-74.602	0	273-323
K ₅	466.497	1614.5	-97.540	0.2471	273-343
K_6	6.822	-6066.9	-2.290	0.0036	273-343
K ₇	-11.563	1769.4	-1.467	0.0024	273-343

 $^{^6}$ Parameter A_{ij} and A_{ji} refer in Aspen $Plus^{TM}$ to the parameter sheet GMELCC, parameter B_{ij} and B_{ji} to GMELCD and parameter α to GMELCN

Table C - 7. Coefficients for dielectric constants for H2O and AMP reported by Dash[30].

Species	А	В
H ₂ O	78.65	31989
PZ	4.253	1532.2
AMP	21.9957	8992.68

 Table C - 8. Antoine equation coefficients for molecular species and ions reported by

 Dash [30].

Components	H ₂ O	CO ₂	PZ	AMP	Ions
А	72.55	72.82921	70.503	20.0032	-1.00E+20
В	-7206.7	-3403.28	-7914.5	-2859.28	0
С	0	0	0	-159.672	0
D	0	9.49E-03	0	0	0
E	-7.1385	-8.56034	-6.6461	0	0
F	4.046E-06	2.91E-16	5.21E-18	0	0
G	2	6	6	0	0

Table C - 9. Coefficients of Henry's constant reported by Dash [30].

Components	CO ₂ -(H ₂ O-PZ-AMP)	CO ₂ -AMP
C ₁	163.4	3.28643
C_2	-820.863	-820.863
C_3	1.69729	1.69729
C_4	-0.002	-0.002

Parameter ⁷	a_{ij}	a _{ji}	b_{ij}	b_{ji}	α
H ₂ O-AMP	3.586	0.374	-327.5	-573.3	0.2
H ₂ O-PZ	1.321	6.996	684.9	-2932	0.2
H ₂ O-H+PZCOO-	7.933	-4.033	0	0	0.2
CO ₂ -AMP	0	0	0	0	0.2
CO ₂ -PZ	0	0	0	0	0.2

Table C - 10. Binary interaction NRTL parameters reported by Dash [30].

Table C - 11. Molecule-ion interaction pair parameters for elecNRTL model reported byDash [30].

Parameter	C _{m,ca}	C _{ca,m}	D _{m,ca}	D _{ca,m}	α
τ H ₂ O-[AMPH ⁺ , PZ(COO ⁻) ₂]	21.859	-11.404	-4298.9	-2250.7	0.2
τ AMP-[PZH ⁺ , HCO ₃ ⁻]	27.940	-6.790	0	0	0.2
τ PZ-[AMPH ⁺ , HCO ₃ ⁻]	3.760	-2.016	0	0	0.2
τ H ₂ O-[AMPH ⁺ , PZCOO ⁻]	8.720	-2.730	0	0	0.2
τ PZ-[AMPH ⁺ , PZCOO ⁻]	0.406	-10.850	0	0	0.2

 Table C - 12. Coefficients for the chemical equilibrium constants used in the elecNRTL

 model reported by Dash [30].

Coefficient	А	В	С	D	T(K)
K ₁	132.899	-13445.9	-22.477	0	273-498
K_2	231.465	-12092.1	-36.782	0	273-498
K ₃	216.049	-12431.7	-35.482	0	273-498
K_4	514.314	-34910.9	-74.602	0	273-323
K ₅	466.497	1614.5	-97.540	0.2471	273-343
K_6	6.822	-6066.9	-2.290	0.0036	273-343
K_7	-11.563	1769.4	-1.467	0.0024	273-343
K ₈	-3.68672	-6754.686	0	0	273-328

 7 Parameter A_{ij} and A_{ji} refer in Aspen $Plus^{TM}$ to the parameter sheet GMELCC, parameter B_{ij} and B_{ji} to GMELCD and parameter α to GMELCN

Table C - 13. Coefficients for dielectric constants for H₂O and AMP reported by Dash [31].

Species	А	В
H ₂ O	78.65	31989
AMP	21.9957	8992.68

Table C - 14. Antoine equation coefficients for molecular species and ions reported byDash [31].

Components	H ₂ O	CO ₂	AMP	Ions
A	72.55	72.82921	20.0032	-1.00E+20
В	-7206.7	-3403.28	-2859.28	0
С	0	0	-159.672	0
D	0	9.49E-03	0	0
E	-7.1385	-8.56034	0	0
F	4.046E-06	2.91E-16	0	0
G	2	6	0	0

Table C - 15. Coefficients of Henry's constant reported by Dash [31].

Components	CO ₂ -H ₂ O	CO ₂ -AMP
C_1	163.8	3.28643
C_2	-8477.711	-820.863
C_3	-21.95743	1.69729
C_4	0.005781	-0.002

Table C - 16. Binary interaction NR	L parameters reported by Dash [31].
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Parameter	a _{ij}	a_{ji}	b _{ij}	b _{ji}	α
H ₂ O-AMP	3.586	0.374	-327.5	-573.3	0.2

Parameter ⁸	C _{m,ca}	C _{ca,m}	D _{m,ca}	D _{ca,m}	α
τ H ₂ O-[AMPH ⁺ , HCO ₃ ⁻]	21.859	-11.404	-4298.9	-2250.7	0.2
τ AMP-[H ₃ O ⁺ , HCO ₃ ⁻]	17.164	-6.9124	0.0	0.0	0.2
τ AMP-[AMPH ⁺ , HCO ₃ ⁻]	17.135	-7.9032	0.0	0.0	0.2
$\tau \operatorname{CO}_2$ -[AMPH ⁺ , HCO ₃ ⁻]	15.0	-8.0	101	101	0.2
τ AMP-[HCO ₃ ⁻ , CO ₃ ²]	10.0	-2.0	101	101	0.2

Table C - 17. Molecule-ion interaction pair parameters for elecNRTL model reported byDash [31].

Table C - 18. Coefficients for the equilibrium constants for elecNRTL model reported byDash [31].

Coefficient	А	В	С	D	T(K)
K_1	132.899	-13445.9	-22.477	0	273-498
K_2	231.465	-12092.1	-36.782	0	273-498
K_3	216.049	-12431.7	-35.482	0	273-498
K_8	-3.68672	-6754.686	0.0	0	273-328

Table C - 19. Coefficients for dielectric constants for H₂O and PZ used in Aspen Example [59].

Species	А	В
H ₂ O	78.54	31989.4
CO_2	1.6	0
PZ	11.2696	8796

 $^{^8}$ Parameter A_{ij} and A_{ji} refer in Aspen $Plus^{TM}$ to the parameter sheet GMELCC, parameter B_{ij} and B_{ji} to GMELCD and parameter α to GMELCN

Components	H ₂ O	CO_2	PZ	Ions
А	72.55	72.82912	70.503	-1.00E+20
В	-7206.7	-3403.28	-7914.5	0
С	0	0	0	0
D	0	0.009491	0	0
Ε	-7.1385	-8.56034	-6.6461	0
F	4.046E-06	2.91E-16	5.2106E-18	0
G	2	6	6	0

Table C - 20. Antoine equation coefficients for molecular species and ions used in AspenExample [59].

Table C - 21. Coefficients of Henry's constant used in Aspen Example [59].

Components	CO ₂ -H ₂ O
C_1	-145.316
C_2	765.8882
C ₃	32.24727
C_4	-0.07395

Table C - 22. Binary interaction NRTL parameters used in Aspen Example [59].

Parameter	a _{ij}	a _{ji}	b _{ij}	b _{ji}	α
H ₂ O-CO ₂	0	0	0	0	0.2
H ₂ O-PZ	0.510999	-0.9099	590.7102	-305.261	0.2

 Table C - 23. Molecule-ion interaction pair parameters for elecNRTL model used in

 Aspen Example [59].

Parameter ⁹	C _{m,ca}	C _{ca,m}	D _{m,ca}	D _{ca,m}	α
default molecule-ion	8	-4	0	0	0.2
τ H ₂ O-[PZH ⁺ , HCO ₃ ⁻]	4.58244	-3.78863	0	0	0.2
τ H ₂ O-[PZH ⁺ , PZCOO ⁻]	10.3136	-5.39625	0	0	0.2

Table C - 24. Coefficients for dielectric constants for H₂O and AMP used in Aspen Example [58].

Species	А	В
H ₂ O	78.51	31989.4
CO_2	1.449	0
AMP	21.04656	8451.2

Table C - 25. Antoine equation coefficients for molecular species and ions used in AspenExample [58].

Components	H ₂ O	CO ₂	AMP	Ions
	(kPa)	(kPa)	(kPa)	
А	65.64224	133.6322	15.155	-1.00E+20
В	-7206.7	-4735	-3472.6	0
С	0	0	-107.32	0
D	0	0	0	0
Ε	-7.1385	-21.268	0	0
F	4.046E-06	0,040909	0	0
G	2	1	0	0

 $^{^9}$ Parameter A_{ij} and A_{ji} refer in Aspen $Plus^{TM}$ to the parameter sheet GMELCC, parameter B_{ij} and B_{ji} to GMELCD and parameter α to GMELCN

-1 abit -20 , Counterents of frem y 5 constant used in Aspen Example (50).
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Components	CO ₂ -H ₂ O	CO ₂ -AMP
C_1	-145.316	19.52
C_2	765.8882	-1205.2
C_3	32.24727	0
C_4	-0.07395	0

Table C - 27. Binary interaction NRTL parameters used in Aspen Example [58].

Parameter	a _{ij}	a _{ji}	b _{ij}	b _{ji}	α
H ₂ O-CO ₂	0	0	0	0	0.2
H ₂ O-AMP	-1.47633	7.086195	-29.7925	-1524.24	0.2

Table C - 28.	Molecule-ion	interaction	pair	parameters	for	elecNRTL	model	used in
Aspen Example	e [58].							

Parameter ¹⁰	C _{m,ca}	C _{ca,m}	D _{m,ca}	D _{ca,m}	α
default molecule-ion	8	-4	0	0	0.2
τ H ₂ O-[AMPH ⁺ , HCO ₃ ⁻]	21.859	-11.404	-4298.9	-2250.7	0.2

 $^{^{10}}$ Parameter A_{ij} and A_{ji} refer in Aspen Plus^{TM} to the parameter sheet GMELCC, parameter B_{ij} and B_{ji} to GMELCD and parameter α to GMELCN

Appendix D: Henry's constants adjustment

Series	Value
HENRY 1	164.63
HENRY 2	165.63
HENRY 3	160.63
HENRY 4	158.63

 Table D - 1. Values for the adjusted Henry's constants.



Figure D - 1. Model predictions for the equilibrium partial pressure of CO₂ in an aqueous solution of 0.6 M PZ for 298 K and different values for the Henry's constant.

Appendix E: Model validation of ternary system AMP-H₂O-CO₂ with regressed pair parameters



Figure E - 1. Model predictions for the equilibrium liquid phase concentration over the loading of CO₂ for an aqueous solution of 2.5 M AMP for 313 K compared to model predictions from Xu [73].



Figure E - 2. Model predictions for the equilibrium liquid phase concentration over the loading of CO₂ for an aqueous solution of 2.5 M AMP for 373 K compared to model predictions from Xu [73].



Figure E - 3. Model predictions for the equilibrium liquid phase concentration over the loading of CO₂ for an aqueous solution of 3.3 M AMP for 298 K compared to ¹³C-NMR spectroscopy studies from Ciftja [57].



Figure E - 4. Model predictions for the equilibrium liquid phase concentration over the loading of CO₂ for an aqueous solution of 3.3 M AMP for 308 K compared to ¹³C-NMR spectroscopy studies from Ciftja [57].



Figure E - 5. Model predictions for the heat of absorption over the loading of CO_2 in an aqueous solution of 2.8 M AMP for 313 K and 353 K compared to exp. data from Mehdizadeh [109].



Figure E - 6. Model predictions for the AMP volatility over the loading of CO_2 in an aqueous solution of 5.0 M AMP for 313 K and 333 K compared to exp. data from Nguyen [76].