# Advancing the large-scale development of PCC processes by providing essential VLE data for aqueous solutions of amines

Charithea Charalambous[a],*, Laura Herraiz[a], Ardi Hartono[b], Hanna Knuutila[b], Susana García[a]

*aResearch Centre for Carbon Solutions, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, United Kingdom*
*bDepartment of Chemical Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway*

**Abstract**

New vapor liquid equilibrium (VLE) ebulliometric data is provided for ternary aqueous 2-Amino-2-methyl-1-propanol (AMP) and Piperazine (PZ) solutions for a range of temperatures (30 ºC, 40 ºC and 50 ºC) and different AMP/PZ ratios (3:1.5 / 4:1 / 6:1). The selected conditions and concentrations are representative of those expected in the water wash systems typically located at the top of an absorption column. The NRTL thermodynamic model in Aspen Plus is used to correlate the VLE data and determine new AMP/PZ binary interaction parameters, leading to an improvement on the prediction of the amine's volatility. The scatter in the experimental data for the AMP and PZ concentrations in the vapor phase however suggests that VLE data are subjected to substantial uncertainty at low temperatures and low amine concentrations. Experimental VLE data also show a small interaction between amine molecules since an increase in the AMP/PZ ratio, for a given AMP and PZ concentration and temperature, does not have a significant effect on either AMP or PZ volatilities.

*Keywords:* $CO_2$ capture; absorption; second generation solvents; vapor liquid equilibrium; NRTL model; amine volatility

## 1. Introduction

Aqueous solutions of alkanolamines are commonly used solvents to remove $CO_2$ from flue gases in amine-based post-combustion carbon capture (PCC) systems. The amines chemically bind $CO_2$ in the absorber where the solvent is directly contacted with the flue gas. The reactions are reversed at high temperatures in the regeneration column where a pure $CO_2$ stream is produced. After regeneration, the lean solvent is recirculated back to the absorption column. Solvent volatility and degradation due to unwanted side reactions are known drawbacks of this technology, as they lead to increased solvent losses and liquid wastes that need to be treated. Increased solvent volatility would result in higher amine concentrations in the gas phase and therefore a more extensive flue gas treatment will be required to remove these amines before being released to the atmosphere. Oxidative amine degradation in presence of oxygen and other reactive contaminants (e.g. nitrogen oxides, sulphur dioxide) and thermal degradation, due to high temperatures during solvent regeneration, can also result in volatile degradation compounds, like ammonia, released to the atmosphere [1], [2]. The direct contact of solvent and flue gas provides a pathway for the carry-over of volatile amine and degradation products into the exhaust gas as vapor, i.e. vapor-based emissions, or suspended liquid, i.e. aerosol-based emissions. There is therefore a need to adopt solvent management and amine emissions abatement strategies to reduce the environmental impact while balancing capital and operational expenses. Several emission mitigation

---

* Corresponding author. Tel.: +44-131-451-8121, *E-mail address:* c.charalambous@hw.ac.uk

measures, including flue gas pre-treatment systems, single water wash, double water wash and acid gas, have been investigated to significantly reduce, or even eliminate, amine emissions to the atmosphere in solvent-based PCC systems [3]. Experimental test campaigns have shown that these wash systems can reduce solvent emissions up to two orders of magnitude in comparison to amine systems without washing systems [4], [5]. In order to optimize the design and operation of solvent emissions abatement strategies, it is necessary to develop accurate rigorous models of these systems.

In addition to minimizing the environmental impact, research activities focus on reducing the energy requirements for high $CO_2$ capture levels to make the PCC process economically viable. Interest has recently grown in mixing alkanolamines to reduce the energy penalty, solvent degradation and solvent losses [4], [6]. The most well-known and broadly used amine in carbon capture systems is monoethanolamine (MEA) due to its low chemical cost, fast reaction rate and high capacity to capture $CO_2$ even at low $CO_2$ partial pressures. However, MEA is moderately volatile and a significant amount of energy is required to strip the $CO_2$ from the rich solvent in the stripper column. Aqueous blends of 2-Amino-2-methyl-1-propanol (AMP) and Piperazine (PZ) merge useful properties from both amines. AMP solutions present a higher $CO_2$ loading capacity and can be regenerated at lower temperatures than MEA solutions. AMP solutions have, however, lower absorption rates for $CO_2$ than MEA solutions. PZ, a cyclic diamine, effectively promotes rapid formation of carbamates and can theoretically absorb two moles of $CO_2$ per mole of amine. Adding PZ to AMP is reported to be an energy and material saving alternative to conventional MEA-based solvents in PCC [4], [5]. Recent studies suggest that aqueous mixtures of AMP and PZ should be considered as the updated benchmark for post-combustion $CO_2$ capture (e.g. European ERA-ACT project ALIGN-CCUS (www.alignccus.eu) and the EU project in the 7th framework program CAESAR).

Vapor-liquid equilibrium (VLE) are fundamental data for developing rigorous thermodynamic models required to design and optimize amine-based gas separation processes. There is however a lack of experimental VLE data at low temperatures and low amine concentrations recorded in the washing sections of the PCC systems [7]–[9]. Existing process models have therefore shown inaccurate predictions of amine emissions, the extent of amine degradation, and consequently lead to inaccurate prediction of the capture plant performance [4], [5].

This work presents new VLE ebulliometric data for unloaded (without $CO_2$) aqueous AMP and PZ solutions at different temperatures (30 ºC, 40 ºC and 50 ºC) and AMP:PZ ratios (3:1.5 / 4:1 / 6:1) representative of those expected in the water wash systems at the top of the absorber column. New VLE data for the ternary system complement existing VLE data in literature [7] and are correlated to further improve the thermodynamic models that will be implemented in rate-based chemical absorption process models for a rigorous design of the absorber columns and, in particular, of the water wash system(s). The ultimate objective of this work is to contribute to the development of robust and reliable predictive simulation tools to reduce the discrepancy between real plant operational data and process modelling results to improve the economics and de-risk large-scale development of PCC processes.

## 2. Methodology

### 2.1. Materials

The purchased chemicals used in the experiments are given in Table 1 and were used without additional purification. The three aqueous solutions with different AMP/PZ ratios were prepared volumetrically and gravimetrically by dissolving the chemical in 1 dm³ of deionized water in flasks over a scale (Mettler Toledo PM1200) at ambient temperature, with an uncertainty of ± 0.05 g. The initial solutions are gradually diluted after reaching the equilibrium to achieve higher dilution ratios.

Table 1. Chemicals used in this work.

| Amine | Abbreviation | CAS number | Purity | Supplier |
|---|---|---|---|---|
| 2-Amino-2-Methyl-1-propanol | AMP | 124-68-5 | ≥0.985[a] | Sigma Aldrich |
| Piperazine | PZ | 110-85-0 | ≥0.992[a] | Sigma Aldrich |

(a) in a mass fraction basis and taken from the Certificate of Analysis CoA from the supplier.

## 2.2. Experimental setup

VLE experiments of the ternary AMP/PZ/H$_2$O system were conducted at three different temperatures 30 ºC, 40 ºC and 50 ºC and for three different AMP/PZ ratios 3:1.5, 4:1 and 6:1, using a modified Swietoslawski ebulliometer. Ebulliometer enables very fast and accurate determination of the vapor-liquid equilibrium of aqueous amines. It is designed for operation at temperatures of below 200 ºC and pressures of a maximum of 1 bar. The temperatures were measured with calibrated Pt-100 resistance thermosensors with an uncertainty of ± 0.05 K. The pressure was measured and controlled with a calibrated DPI520 rack mounted pressure controller (Druck, Germany) with an uncertainty of ±0.3 kPa. The measured temperature corresponds to the equilibrium conditions established at the given total pressure and the compositions of the liquid and vapor phases. The system was considered to be at equilibrium when no change in pressure and temperature was observed, and the vapor leaving the heater and entering the equilibrium chamber was at a constant rate. The detailed experimental set up and procedures can be found in previous work [10]. The liquid-phase samples of the mixtures of amines are analyzed by advanced analytical methods including titration and liquid chromatography with mass spectrometry (LC-MS), allowing for quantification of the content of each amine in the liquid phase and in the condensed gas phase (volatility). The LC-MS analyses were performed on an LC–MS/MS system, 6460 Triple Quadrupole Mass Spectrometer coupled with 1290 Infinity LC Chromatograph and Infinity Autosampler 1200 Series G4226A from the supplier Agilent Technologies [11]. The LC-MS method reports an average deviation of 3% [12]. The maximum propagation error for concentrations was estimated and given as $\Delta x \pm$ 3%. Minor uncertainty sources came from pressure and temperature measurements, and therefore the accuracy of the results is limited by the precision of the analytical methods used for the sample analysis.

## 2.3. Thermodynamic model

The ebulliometer experiments provide P-T-x-y data for the ternary system and, with these data, we use a thermodynamic model to calculate the activity coefficients of each component (i.e., AMP, PZ and H$_2$O) in the mixture. The partial pressures of AMP and PZ in the vapor phase at equilibrium can then be calculated according to Equation (1). Here $x_i$, $y_i$, $P_T$, $P_i^S$, and $\emptyset_i$ are the liquid mole fraction, vapor mole fraction, total pressure of the solution, saturation pressure of pure substance, and the Poynting factor, respectively. The saturation pressure of pure components (i.e., AMP, PZ and H$_2$O) are evaluated according to the correlations for the Antoine equation presented in Table 2, which are taken from Hartono et al. [13].

$$y_i \cdot P_T \cdot \emptyset_i = \gamma_i \cdot x_i \cdot P_i^S \tag{1}$$

The NRTL thermodynamic model for multi-component mixtures is considered in this study to interpret the data since it has been proved suitable for predicting experimental VLE data of various amine systems [7]. The local interaction energy parameters in the NRTL/eNRTL model, $G_{ij}$ and $\tau_{ij}$, are expressed as a function of temperature according to Equation (2) and Equation (3). The model requires 12 binary interaction parameters (listed in Table 3), $a_{ij}$ and $b_{ij}$, to be calculated when the non-randomness parameter $\alpha_{ij}$ is set to a fixed value of 0.2.

$$G_{ij} = \exp\left(-\alpha_{ij} \cdot \tau_{ij}\right) \tag{2}$$

$$\tau_{ij} = a_{ij} + b_{ij}/T ; \quad \tau_{ii} = \tau_{jj} = \tau_{kk} = 0 \tag{3}$$

The binary interaction parameters for AMP/$H_2O$ and PZ/$H_2O$ are regressed in previous work by Hartono et al. [13] using experimental VLE data of the respective binary systems, showing a good agreement between the model results and the experimental data for the total pressure, the amine partial pressures, and the activity coefficients. These binary interaction parameters are used here for additional modelling work of the ternary AMP/PZ/$H_2O$ system. The Aspen Plus Data Regression System (DRS) determines the binary interaction parameters by fitting to experimental data using the Britt-Luecke's Generalized Least-Squares method based on the maximum likelihood principle as the regression algorithm.

Table 2. Correlations used in the ternary NRTL model [13].

| No. | Correlation |
|---|---|
| 1 | $\ln(P_{H_2O}^s/\text{Pa}) = 73.649 - 7258.2/T - 7.3037 \cdot \ln(T) + 4.1653 \cdot 10^{-6} \cdot T^2$ |
| 2 | $\ln(P_{AMP}^s/\text{kPa}) = 7.1405 - 1858.4/(T - 74.9)$ |
| 3 | $\ln(P_{PZ}^s/\text{kPa}) = 5.9832 - 1215.77/(T - 113.56)$ |

## 3. Results

### 3.1. Modeling results for the unloaded ternary AMP/PZ/$H_2O$ system

The binary interaction parameters for AMP/PZ are indirectly obtained from fitting ternary VLE data for the AMP/PZ/$H_2O$ system, while keeping the optimum values for the binary interaction energies of AMP/ $H_2O$ and PZ/$H_2O$, since data for the pure AMP/PZ blends are not available. New VLE data at 30 ºC, 40 ºC and 50 ºC for AMP/PZ ratios of 3:1.5, 4:1 and 6:1 (experimentally determined in this work) and VLE data at 60 ºC, 70 ºC, 80 ºC, 90 ºC and 100 ºC (previously reported in literature [13]) are used in the regression of the NRTL thermodynamic model in Aspen Plus. New experimental VLE data (see dotted points in Fig. 1) cover a range of amine concentrations in liquid phase from 0.045 %vol to 18.64 %vol for AMP and from 0.013 %vol to 3.44 %vol for PZ, and a range of amine concentration in vapor phase from 0.0023 %vol to 0.31 %vol for AMP and from 0.0003 %vol to 0.039 %vol for PZ. Experimental VLE data shows an increased amine volatility at high temperature and high amine concentrations. Increasing the AMP/PZ ratio does not seem to have a significant effect on either AMP volatility or PZ volatility, which suggests a small interaction between amine molecules for the range of amine concentrations investigated here. The scatter in experimental data might be explained by the large uncertainty in the analyses; VLE data are difficult to obtain at low temperatures and low total pressures. Moreover, PZ volatility is considerably low and close to the detection limit of the instrument and therefore difficult to measure with high accuracy.

Fig. 1 shows the experimental AMP and PZ volatility (dots) obtained in this work for the unloaded ternary systems at 30 ºC, 40 ºC and 50 ºC and the predicted values (lines) obtained by the NRTL model. Fig. 2 shows the experimental AMP and PZ volatility (dots) provided in [7] for the unloaded ternary system at 60 ºC, 70 ºC, 80 ºC, 90 ºC and 100 ºC and the predicted values (lines) obtained by the NRTL model. Existing Aspen Plus models consider default values for the AMP/PZ binary interaction parameters as zero. The default NRTL model predicts higher volatility for both AMP and PZ than that experimentally observed (see dashed lines in Fig.1). The deviation is more significant at low temperatures, e.g. from 30 to 60ºC, and high amine concentrations in the aqueous solution, e.g. above 1 %vol for both PZ and AMP. This suggests the need of regressing the four binary interaction parameters for the AMP/PZ system using experimental VLE data. The set of VLE data experimentally obtained has shown insufficient to regress the four parameters within the ranges of physical validity and/or with statistical significance (i.e. low standard deviations), so new experimental tests will be conducted at a later stage. The AMP(1)/PZ(2) parameters, $a_{12}$ and $b_{12}$, are therefore set to zero and the PZ(2)/AMP(1) parameters are regressed. This approach gave a slightly better prediction of the experimental data (see dashed and continuous lines in Fig. 1 and Fig. 2). Table 3 presents the binary interaction parameters obtained in the regression and the amine volatility predicted by the NRTL model is illustrated in Fig. 1 and Fig. 2 (see continuous green and orange lines) for a range of temperatures and for 1:1 AMP/PZ ratio. The NRTL thermodynamic model shows a good prediction of the amine volatility and total pressure (continuous lines), yet the

deviation of the model results from the experimental data expressed as absolute average relative deviations (AARD) is still relatively- high, ca. 28% for AMP partial pressure and 58% for PZ partial pressure, due to the scatter in experimental data. Further analysis will use new experimental VLE data for the $CO_2$ unloaded and loaded AMP/PZ/$H_2O$ systems to regress the AMP/PZ binary interaction parameters and assess the effect of the final eNRTL/NRTL thermodynamic model in Aspen Plus for the quaternary system. We will also explore the possibility of using two models; one in the absorber, where amine concentrations are higher and one in the water wash, where amine concentrations are much lower.

Table 3. Binary interaction parameters of AMP(1) + PZ(2) + $H_2O$(3) for the NRTL model.

| System | Parameter | Quantity | Parameter | Quantity |
|---|---|---|---|---|
| AMP(1) + $H_2O$(3) [a] | $a_{13}$ | -0.34 | $a_{31}$ | 4.49 |
| | $b_{13}$ | -546.90 | $b_{31}$ | -372.00 |
| PZ(2) + $H_2O$(3) [a] | $a_{23}$ | -0.60 | $a_{32}$ | 5.32 |
| | $b_{23}$ | -698.51 | $b_{32}$ | -1280 |
| AMP(1) + PZ(2) [b] | $a_{12}$ | 0 | $a_{21}$ | 19.10 |
| | $b_{12}$ | 0 | $b_{21}$ | -7049.14 |

(a)     Regressed in Hartono et al. 2013 [13]
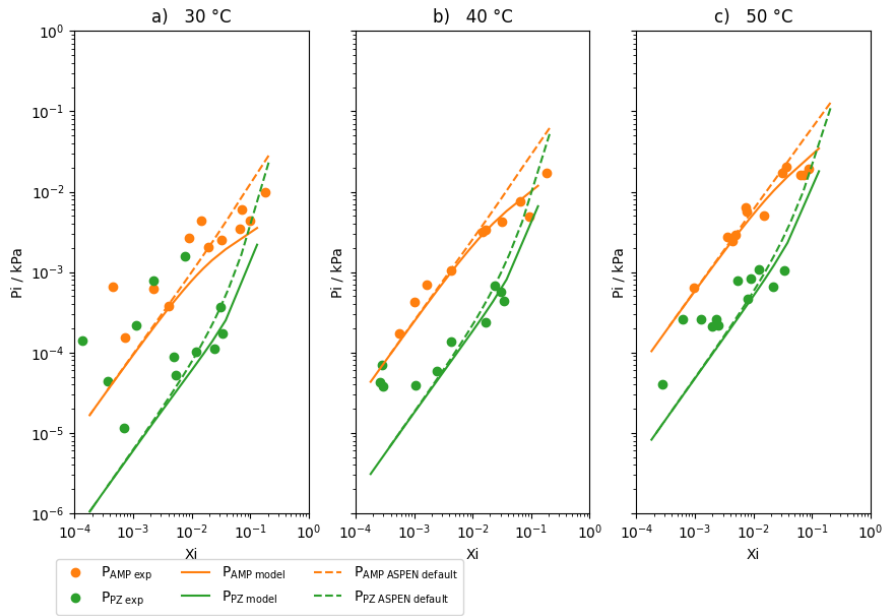(b)     Regresses in this work

Fig. 1. Volatility of AMP and PZ and representation of the NRTL model for the unloaded ternary system at different temperatures: (a) 30 ºC, (b) 40 ºC and (c) 50 ºC and AMP:PZ ratios of 3:1.5/4:1/6:1. Lines: NRTL model in Aspen. ● Experimental data in this work.
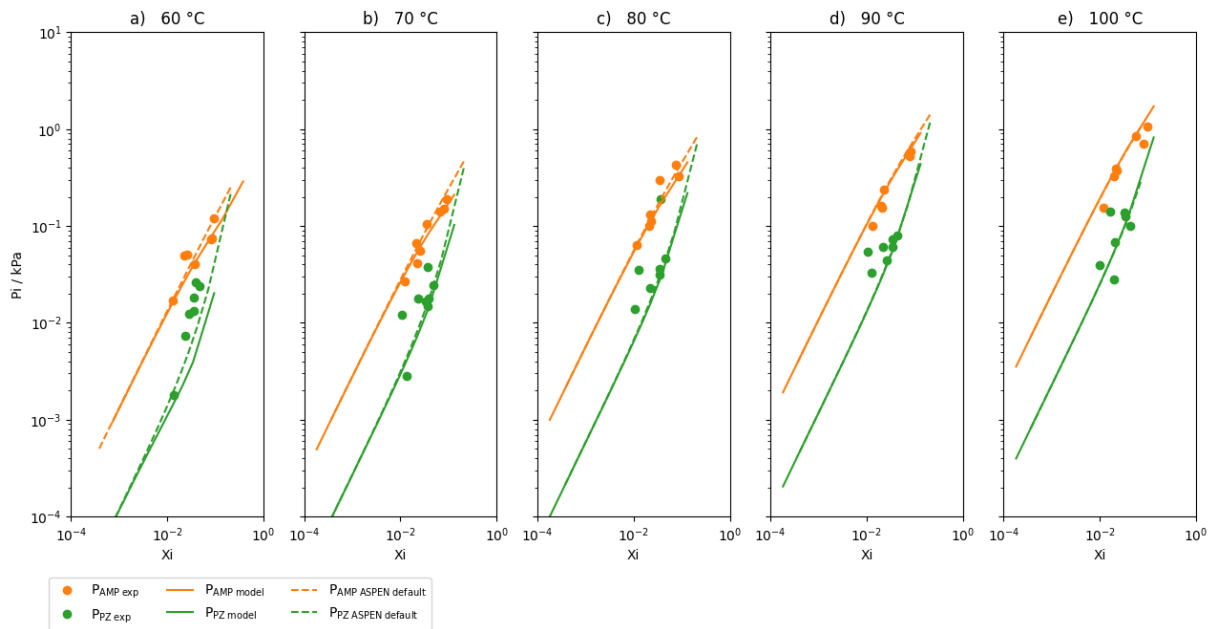


Fig. 2. Volatility of AMP and PZ and representation of the NRTL model for the unloaded ternary system at different temperatures:(a) 60 ºC, (b) 70 ºC, (c) 80 ºC, (d) 90 ºC and (e) 100 ºC. Lines: NRTL model in Aspen. ● Experimental data in [7].

## 4. Conclusions

New vapor liquid equilibrium (VLE) ebulliometric data are presented for the ternary aqueous AMP and PZ solutions for a range of temperatures (30 ºC, 40 ºC and 50 ºC) and different AMP/PZ ratios (3:1.5 / 4:1 / 6:1) representative of those expected in the water wash section, typically located at the top the absorption columns in PCC systems. Experimental results show that AMP is significantly more volatile than PZ, and the determination of PZ concentrations in the vapor phase have proven to be very challenging at low temperatures as the VLE data obtained for PZ are more scattered than those obtained for AMP. The scatter in experimental data for AMP and PZ vapor phase concentration might be explained by the large uncertainty in the analyses; VLE data are difficult to obtain at low temperatures and low total pressures. No significant effect on the volatility of either AMP or PZ is observed when the AMP/PZ ratio increases within the range of amine concentrations investigated in this study, which suggest a weak interaction between amine molecules.

Existing Aspen Plus models consider default zero values for the AMP/PZ binary interaction parameters, yet the NRTL model predicts higher amine volatility, for both AMP and PZ, than the experimentally observed one. New binary interaction parameters between the two amines (AMP/PZ) are regressed for the NRTL thermodynamic model in Aspen Plus. The NRTL model presents a good correlation of the experimental data for a wide range of temperatures and AMP/PZ ratios. The statistical significance of the new binary interaction parameters on the NRTL thermodynamic model describing the quaternary $AMP/PZ/CO_2/H_2O$ system is being addressed in upcoming work.

## References

[1] A. Rieder *et al.*, "Understanding Solvent Degradation: A Study from Three Different Pilot Plants within the OCTAVIUS Project," in *Energy Procedia*, 2017, vol. 114, pp. 1195–1209. doi: 10.1016/j.egypro.2017.03.1376.

[2] T. Spietz, T. Chwoła, A. Krótki, A. Tatarczuk, L. Więcław-Solny, and A. Wilk, "Ammonia emission from $CO_2$ capture pilot plant using aminoethylethanolamine," *International Journal of Environmental Science and Technology*, vol. 15, no. 5, pp. 1085–1092, May 2018, doi: 10.1007/s13762-017-1475-z.

[3] P. Moser *et al.*, "Demonstrating emission reduction - Results from the post-combustion capture pilot plant at Niederaussem," in *Energy Procedia*, 2014, vol. 63, pp. 902–910. doi: 10.1016/j.egypro.2014.11.100.

[4] P. Moser *et al.*, "ALIGN-CCUS: Results of the 18-month test with aqueous AMP/PZ solvent at the pilot plant at Niederaussem – solvent management, emissions and dynamic behavior," *International Journal of Greenhouse Gas Control*, vol. 109, Jul. 2021, doi: 10.1016/j.ijggc.2021.103381.

[5] P. Moser *et al.*, "Results of the 18-month test with MEA at the post-combustion capture pilot plant at Niederaussem – new impetus to solvent management, emissions and dynamic behaviour," *International*

*Journal of Greenhouse Gas Control*, vol. 95, no. September 2019, p. 102945, 2020, doi: 10.1016/j.ijggc.2019.102945.

[6]     Y. Artanto *et al.*, "Pilot-scale evaluation of AMP/PZ to capture $CO_2$ from flue gas of an Australian brown coal-fired power station," *International Journal of Greenhouse Gas Control*, vol. 20, pp. 189–195, 2014, doi: 10.1016/j.ijggc.2013.11.002.

[7]     A. Hartono, M. Saeed, A. F. Ciftja, and H. F. Svendsen, "Binary and ternary VLE of the 2-amino-2-methyl-1-propanol (AMP)/piperazine (Pz)/water system," *Chemical Engineering Science*, vol. 91, pp. 151–161, Mar. 2013, doi: 10.1016/j.ces.2013.01.015.

[8]     H. Li, P. T. Frailie, G. T. Rochelle, and J. Chen, "Thermodynamic modeling of piperazine/2-aminomethylpropanol/$CO_2$/water," *Chemical Engineering Science*, vol. 117, pp. 331–341, Sep. 2014, doi: 10.1016/j.ces.2014.06.026.

[9]     R. R. Wanderley, D. D. D. Pinto, and H. K. Knuutila, "Investigating opportunities for water-lean solvents in $CO_2$ capture: VLE and heat of absorption in water-lean solvents containing MEA," *Separation and Purification Technology*, vol. 231, Jan. 2020, doi: 10.1016/j.seppur.2019.115883.

[10]    I. Kim, "Heat of reaction and VLE of post combustion $CO_2$ absorbents," NTNU: Norwegian University of Science and Technology, Norway, 2009.

[11]    A. Hartono, F. Saleem, M. W. Arshad, M. Usman, and H. F. Svendsen, "Binary and ternary VLE of the 2-(diethylamino)-ethanol (DEEA)/3-(methylamino)-propylamine (MAPA)/water system," *Chemical Engineering Science*, vol. 101, pp. 401–411, Sep. 2013, doi: 10.1016/j.ces.2013.06.052.

[12]    I. Kim, K. A. Hoff, E. T. Hessen, T. Haug-Warberg, and H. F. Svendsen, "Enthalpy of absorption of $CO_2$ with alkanolamine solutions predicted from reaction equilibrium constants," *Chemical Engineering Science*, vol. 64, no. 9, pp. 2027–2038, May 2009, doi: 10.1016/j.ces.2008.12.037.

[13]    A. Hartono, R. Ahmad, H. F. Svendsen, and H. K. Knuutila, "New solubility and heat of absorption data for $CO_2$ in blends of 2-amino-2-methyl-1-propanol (AMP) and Piperazine (PZ) and a new eNRTL model representation," *Fluid Phase Equilibria*, vol. 550, Dec. 2021, doi: 10.1016/j.fluid.2021.113235.