



Experimental VLE data for the AMP/PZ/H₂O system under relevant water wash conditions for carbon capture applications

Charithea Charalambous^a, Laura Herraiz^a , Ardi Hartono^b, Hanna K. Knuutila^b , Susana Garcia^{a,*}

^a Research Centre for Carbon Solutions, School of Engineering and Physical Sciences, Heriot-Watt University, EH14, 4AS Edinburgh, United Kingdom

^b Department of Chemical Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway

ARTICLE INFO

Keywords:

Vapor-liquid equilibrium
eNRTL
AMP
PZ
Volatility

ABSTRACT

New vapour liquid equilibrium (VLE) ebulliometric data for 2-Amino-2-methyl-1-propanol (AMP) and Piperazine (PZ) aqueous solutions are presented in this work for a range of temperatures, 30°C, 40°C and 50°C, and AMP:PZ molar ratios of 3:1.5/4:1/6:1 representative of those expected in water wash systems typically located at the top of absorber columns as an effective emission mitigation strategy in post-combustion carbon capture. The scatter in experimental data for AMP and PZ partial pressures suggests that obtaining VLE experimental data at low temperatures and low amine concentrations is challenging, despite its necessity. Experimental VLE data also suggest that an increase in the AMP/PZ ratio, as typically encountered in water wash processes, does not notably impact the volatility of each amine. The newly developed NRTL thermodynamic models in Aspen Plus (Yi et al., 2024) and Matlab (Hartono et al., 2021a) for the quaternary system AMP/Pz/H₂O/CO₂ show improvements in predicting the volatility of amines.

1. Introduction

Amine-based post-combustion carbon capture (PCC) stands out as the most mature and widely adopted technology for mitigating CO₂ emissions from power plants and various industrial sources. Concerns arise regarding potential atmospheric emissions of the solvent amines and their degradation products, specifically falling within chemical classes associated with environmental risks. Notably, nitrosamines and nitramines known for their documented adverse effects on human health and the environment, are of particular concern in this context (Rieder et al., 2017; Spietz et al., 2018). Solvent emissions and degradation also lead to increased solvent losses and generate waste streams that require further treatment. Consequently, there is a pressing need to implement solvent management and emissions mitigation strategies, aiming to minimise environmental impact while maintaining a balance between capital and operational expenses (Moser et al., 2014; Weir et al., 2023). Emissions mitigation technologies including single water wash, dry bed, double water wash and acid gas downstream of the absorber column and pre-treatment of the flue gas upstream of the absorber column (e.g. Brownian Demister Unit (BDU), turbulent pre-treatment) have been proven to reduce the volatile and aerosol emissions even below the

detection threshold for a range of flue gas characteristics (Moser et al., 2020; Moser et al., 2021). In particular, Moser et al. (Moser et al., 2020; Moser et al., 2021) demonstrated that a single water wash has the potential to decrease solvent emissions by up to two orders of magnitude compared to amine technologies without washing systems.

In addition to addressing environmental concerns, current research efforts are directed towards minimising the energy requirements for regeneration at high CO₂ capture rates, aiming to enhance the economic viability of carbon capture and storage (CCS) processes. An emerging technology in this domain involves the absorption of CO₂ in aqueous blends of 2-Amino-2-methyl-1-propanol (AMP) and Piperazine (PZ). Sterically hindered amines like AMP offer high absorption capacity and can be blended with a high reaction rate promoter such as PZ – a cyclic diamine known to effectively facilitate the rapid formation of carbamates. PZ can theoretically absorb two moles of CO₂ per mole of amine. Recent studies propose that PZ-activated AMP should be considered as the updated benchmark for PCC, as evidenced by contributions from projects like the European ERA-ACT project ALIGN-CCUS and the EU project CESAR in the 7th framework program (Feron et al., 2020). This solvent blend therefore combines advantageous properties from both amines, demonstrating superior characteristics compared to the

* Corresponding author.

E-mail address: s.garcia@hw.ac.uk (S. Garcia).

<https://doi.org/10.1016/j.ces.2024.120992>

Received 19 June 2024; Received in revised form 12 November 2024; Accepted 24 November 2024

Available online 11 December 2024

0009-2509/© 2024 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Table 1
Chemicals used in this work.

Amine	Abbreviation	CAS number	Purity	Supplier
2-Amino-2-Methyl-1-propanol	AMP	156-87-6	≥ 0.990 [*]	Sigma Aldrich
Piperazine	PZ	110-85-0	≥ 0.992 [*]	Sigma Aldrich

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

incumbent technology using monoethanolamine (MEA) with respect to regeneration energy, absorption capacity, degradation, and corrosion (Spek et al., 2016; Artanto et al., 2014).

Achieving a suitable design and effective control of emission mitigation strategies hinges on the development of thermodynamic models coupled with kinetic models in process simulation software. The incorporation of vapor–liquid equilibrium (VLE) experimental data is crucial for improving thermodynamic models, which play a pivotal role in evaluating the techno-economic performance of amine-based carbon capture technologies. Unfortunately, there is a notable scarcity of VLE data, particularly at low temperatures and low amine concentrations recorded in the washing sections of capture plants (Hartono et al., 2021a; Wanderley et al., 2020; Li et al., 2014). A recent study from (Maxime et al., 2024) provides VLE data for the CO₂-loaded system at low concentrations, highlighting that low-concentration data for fitting VLE model are needed to correctly predict the volatility of amine solvent systems. The absence of comprehensive experimental VLE data poses a challenge as existing process models exhibit inaccuracies in predicting amine emissions, the extent of amine degradation, and subsequently, the overall performance of the capture plant. Addressing this gap in experimental data is crucial for refining and validating process models, ensuring their reliability in guiding the design and control of emission mitigation strategies in amine-based carbon capture systems.

In this study, novel VLE ebulliometric data for unloaded aqueous AMP and PZ solutions are introduced for the first time. These data were acquired at different temperatures (30 °C, 40 °C and 50 °C) and AMP:PZ molar ratios of 3:1.5, 4:1, and 6:1. The selected temperatures and concentrations are representative of those anticipated in water wash systems typically located at the top of absorber columns. The newly generated VLE data for the ternary system complement the existing VLE data presented by Hartono et al. (2013). These data are then compared to predicted values with newly developed eNRTL thermodynamic models for CO₂ absorption into aqueous solutions of AMP and PZ on Aspen Plus (Yi et al., 2024) and Matlab (Hartono et al., 2021a). These models are being used in rate-based chemical absorption process models for a rigorous design of absorber columns and water wash systems. The overarching goal of this research is to contribute to the development of robust and reliable predictive simulation tools. These tools aim to minimize the disparity between plant operational data and emission predictions, ultimately enhancing the economic feasibility and reducing the risks associated with the large-scale deployment of PCC technologies.

2. Methodology

2.1. Material

The purchased chemicals used in the experiments are given in Table 1 and were used without additional purification. The three aqueous amine solutions with different AMP:PZ molar ratios (i.e., 3 M AMP + 1.5 M PZ, 4 M AMP + 1 M PZ, and 6 M AMP + 1 M PZ) 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

Table 2
The prepared aqueous solutions for experiments.

No.	Solution name	Molarity mol/dm ³ solution	Molality mol/kg water	Mass % 100 % kg/kg total AMP:PZ
1	3 M AMP + 1.5 M PZ	3.0:1.5	5.0:2.5	26.7:12.9
2	4 M AMP + 1 M PZ	4.0:1.0	7.2:1.8	35.7:8.6
3	6 M AMP + 1 M PZ	6.0:1.0	15.8:2.6	53.5:8.6

unit conversions of the prepared solutions to molality and mass % are provided in Table 2. All other solutions were progressively diluted from these three initial solutions of AMP and PZ to achieve lower amine concentrations while maintaining a constant AMP:PZ molar ratio (i.e., 3:1.5, 4:1, and 6:1). To vary the composition of the liquid-phase, some solution in the system was removed and replaced with water.

3. Experimental setup

VLE experiments of the ternary AMP/PZ/H₂O system were conducted at three different temperatures (i.e., 30 °C, 40 °C, and 50 °C) and for three different AMP:PZ molar ratios (i.e., 3:1.5, 4:1, and 6:1) using a modified Swietoslawski ebulliometer. Ebulliometry enables very fast and accurate determination of the vapor–liquid equilibrium of aqueous amines. It is designed for operation at temperatures of below 200 °C and pressures up to a maximum of 1 bar. The temperatures were measured with calibrated Pt-100 resistance thermosensors with an uncertainty of $u(T) \pm 0.15$ °C. The pressure was measured and controlled with a calibrated DPI520 rack mounted pressure controller (Druck, Germany) with an uncertainty of $u(P) \pm 0.15$ 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 in 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 description of the experimental set up and experimental procedure can be found in previous work by Kim et al. (2009, 2008). The gas phase is condensed, allowing liquid-phase sampling of both the liquid and gas phases. The samples containing mixtures of amines were analysed by liquid chromatography with mass spectrometry (LC-MS), enabling quantification of the content of each amine in the liquid and the condensed gas phases (volatility). The LC-MS method reports an average deviation of 5 % (Vevelstad et al., 2013). The limit of detection was reported at 1 mg/kg, well above amine concentrations in the gas phase (Silva et al., 2012). The maximum propagation error for concentrations was estimated and given as $u(x) \pm 5$ %. 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.

4. Thermodynamic model

The ebulliometer experiments provide P-T-x-y data for the ternary system which are typically used in the thermodynamic model to calculate the activity coefficients of each component (i.e., AMP, PZ, and H₂O) in the mixture. The partial pressures of AMP and PZ in the vapor phase at equilibrium can then be calculated according to Equation (1). The left hand-side represents the vapor phase, where P_T is the total pressure of the solution, y_i is the component i mole fraction, and ϕ_i is the gas phase fugacity coefficient of component i . The right hand-side represents the liquid phase, where x_i is the component i mole fraction, γ_i is the activity coefficient for component i , P_i^S is the saturation vapor pressure of pure substance, ϕ_i^S is the liquid phase fugacity coefficient, and ψ_i is the

Table 3
Correlations used in the ternary NRTL model.

No.	Correlation	Source
1	$1 \ln(P_{H_2O}^S/Pa) = 73.649 - 7258.2/T(K) - 7.3037 \cdot \ln T(K) + 4.1653 \times 10^{-6} \cdot T(K)^2$	(DIPPR-801 2004)
2	$2 \log(P_{AMP}^S/kPa) = 7.1405 - 1858.4/(T(K) - 74.9)$	(Hartono et al., 2020)
3	$3 \log(P_{PZ}^S/kPa) = 5.9832 - 1215.77/(T(K) - 113.56)$	(Hartono et al., 2021b)

Poynting factor. The saturation pressure of pure components is evaluated according to the correlation for the Antoine equation (Hartono et al., 2021a) as presented in Table 3. The saturation pressure of pure PZ and the binary interaction parameters for PZ/H₂O were regressed simultaneously using VLE data for the binary system, including solid–liquid equilibrium, and calorimetric data. For further details the reader is referred to work in Hartono et al., 2020.

$$y_i \cdot P_T \cdot \varphi_i = \gamma_i \cdot x_i \cdot P_i^S \cdot \phi_i^S \cdot \psi_i \quad (1)$$

The NRTL/eNRTL thermodynamic model for a multi-component mixture is considered in this work to interpret the data since it has been proven suitable for predicting experimental VLE data of various amine systems. The local energy interaction parameters in the NRTL/eNRTL model, G_{ij} and τ_{ij} , are expressed as function of temperature

according to Equations (2) and (3). The model requires binary interaction parameters, a_{ij} and b_{ij} , for molecule–molecule and molecule anion/cation pairs to be calculated when the non-randomness parameter α_{ij} is set to a fixed value of 0.2 (Prausnitz et al., 1998).

$$G_{ij} = \exp(-\alpha_{ij} \cdot \tau_{ij}) \quad (2)$$

$$\tau_{ij} = a_{ij} + b_{ij}/T; \tau_{ij} = \tau_{ji} = \tau_{kk} = 0 \quad (3)$$

The eNRTL/NRTL thermodynamic models for the quaternary system AMP/PZ/H₂O/CO₂ used here has been developed in Aspen Plus v12 and Matlab. The methodology followed to fit the binary interaction parameters of the eNRTL thermodynamic models and validate the model against a wide range of experimental VLE data is detailed in previous work by some of the authors in this paper, Yi et al., 2024 and Hartono et al., 2021a. The binary interaction parameters for the binary AMP/H₂O and PZ/H₂O systems are first regressed using experimental data of the amine partial pressure in amine aqueous solutions. Additional binary interaction parameters for the ternary systems AMP/H₂O/CO₂ and PZ/H₂O/CO₂ are regressed using experimental VLE data of the total pressure and the CO₂ partial pressure for a wide range of CO₂ loadings at different amine concentrations and temperatures. The remaining binary interaction parameters between species only present in the quaternary system AMP/PZ/H₂O/CO₂ are then regressed using additional VLE data of the total pressure and CO₂ partial pressure obtained for aqueous blends of AMP/PZ (Hartono et al., 2021a; Brüder et al., 2011; Tong

Table 4
Ternary VLE data for AMP(1) + PZ(2) + H₂O(3) system at different temperatures.

T (°C)	P (kPa)	Liquid phase					Vapor phase				
		AMP:PZ	AMP(g/kg)	PZ(g/kg)	xAMP(mol/mol)	xPZ(mol/mol)	AMP(mg/kg)	PZ(mg/kg)	yAMP(ppmv)	yPZ(ppmv)	
30	3.6	4	334.5	80.2	0.1003	0.0249	6059	147	1233	31	
30	4.1	4	87.9	21.3	0.0195	0.0049	2492	104	506	22	
30	3.9	4	173.3	41.4	0.0422	0.0104	4984	119	1011	25	
30	4.1	4	46.0	11.1	0.0097	0.0024	1222	40	247	8	
30	3.2	6	491.4	79.8	0.1816	0.0305	15,033	544	3083	115	
30	3.8	6	270.2	42.7	0.0726	0.0119	7888	130	1608	27	
30	3.9	6	141.7	22.4	0.0329	0.0054	3163	65	642	14	
31	4.2	6	19.6	3.3	0.004	0.0007	448	13	91	3	
30	4.1	6	67.4	10.8	0.0145	0.0024	2625	50	532	11	
30	4.2	6	37.8	6.1	0.0079	0.0013	878	19	178	4	
30	4.2	6	10.7	1.7	0.0022	0.0004	445	12	90	3	
40	6.5	2	237.0	118.7	0.0661	0.0343	5752	319	1171	67	
40	6.8	2	131.9	68.4	0.0316	0.017	3019	167	613	35	
40	7.2	2	70.5	34.7	0.0155	0.0079	1926	91	390	19	
40	7.2	2	19.9	10.1	0.0041	0.0022	583	33	118	7	
40	7.3	2	6.8	3.3	0.0014	0.0007	258	19	52	4	
40	6.5	4	320.2	78.2	0.0942	0.0238	3688	505	749	106	
40	7.1	4	77.3	18.6	0.0169	0.0042	2316	91	470	19	
40	7.3	4	20.5	5.0	0.0042	0.0011	701	26	142	5	
40	7.0	4	156.9	37.4	0.0375	0.0092	5581	168	1133	35	
40	7.2	4	40.1	9.4	0.0084	0.002	1257	41	254	9	
40	5.6	6	498.9	79.5	0.1864	0.0307	15,092	487	3095	103	
40	7.2	6	68.5	10.9	0.0148	0.0024	2178	39	442	8	
40	7.3	6	36.2	5.8	0.0076	0.0012	1408	36	285	8	
50	11.7	2	230.8	115.9	0.0638	0.0331	6846	425	1395	90	
50	12.2	2	21.0	10.6	0.0044	0.0023	989	101	200	21	
50	12.0	2	69.9	34.9	0.0154	0.008	2084	186	423	39	
50	12.2	2	23.6	11.8	0.0049	0.0025	1174	86	238	18	
50	11.8	2	121.3	61.0	0.0287	0.0149	7035	490	1430	103	
50	12.2	2	7.7	3.8	0.0016	0.0008	268	21	54	4	
50	11.8	4	150.8	37.3	0.0358	0.0092	8505	339	1735	72	
50	12.1	4	36.8	9.1	0.0077	0.002	2318	84	470	18	
51	12.3	3	4.7	1.3	0.001	0.0003	254	16	51	3	
50	12.0	4	75.4	18.3	0.0165	0.0041	5345	202	1085	42	
49	12.2	4	18.7	4.5	0.0039	0.001	1201	56	243	12	
49	12.2	4	7.7	1.9	0.0016	0.0004	573	28	116	6	
50	12.1	6	133.4	22.4	0.0307	0.0053	6879	311	1401	66	
50	11.9	6	267.1	44.6	0.0717	0.0124	6659	434	1356	92	
50	12.2	6	35.3	5.9	0.0074	0.0013	2598	100	527	21	
50	12.2	6	71.8	11.2	0.0155	0.0025	3028	114	614	24	
50	12.3	6	7.6	1.2	0.0015	0.0002	308	7	62	1	

Standard (u), relative (ur) and combined (U) uncertainties: $u(T) = 0.15$ °C, $u(P) = 0.15$ kPa, $ur(AMP) = 5\%$, $ur(PZ) = 5\%$, $U(P_{AMP}) \approx 6\%$, and $U(P_{PZ}) \approx 6\%$.

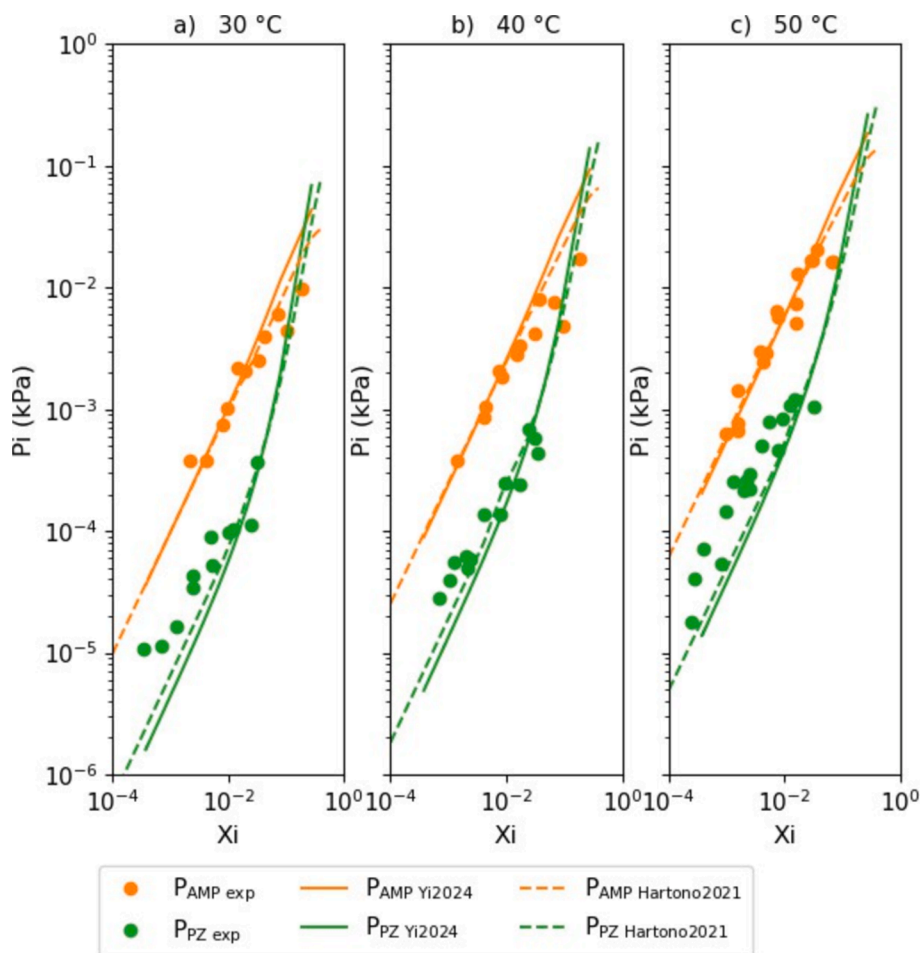


Fig. 1. Volatility of AMP and PZ and representation of the NRTL model for the unloaded AMP/PZ/H₂O system at different temperatures: (a) 30 °C, (b) 40 °C, and (c) 50 °C and AMP:PZ ratios of 3:1.5, 4:1, and 6:1. • Experimental data in this work. Continuous Line: NRTL model in Aspen Plus (Yi et al., 2024). Dashed line: NRTL model in Matlab (Hartono et al., 2021a).

et al., 2013; Li et al., 2013; Dash et al., 2011). The Aspen Plus Data Regression System determines the binary interaction parameters by fitting them to experimental data using the Britt-Luecke's Generalized Least-Squares method based on the maximum likelihood principle as the regression algorithm (Britt and Luecke, 1973).

The binary interaction parameters for AMP/PZ could be indirectly obtained from fitting ternary VLE data for the AMP/PZ/H₂O system obtained in this work, while keeping the optimum values for the binary interaction energies for AMP/H₂O and PZ/H₂O, as described before. Adding the set of VLE experimental data presented in this paper, however, led to an over-fitted thermodynamic model that would not predict well the CO₂ solubility at low CO₂ partial pressures. The AMP/PZ binary interaction parameters are therefore set to zero (i.e., default value in Aspen Plus) in the NRTL/eNRTL thermodynamic model to assess the deviation between the predicted values and the experimental data of the AMP and PZ volatility measured in this work.

As mentioned, the primary goal of this study is to provide VLE experimental data and quantitative values of amine volatility under operating conditions relevant for water wash systems. The VLE experimental data obtained in this study are employed not for regression purpose but rather for the comparison and validation of predicted amine emissions by the eNRTL thermodynamic models. This method aims to advance the development of more refined thermodynamic models that can be integrated into a robust rate-based model of the CO₂ capture process, with a specific focus on designing amine emissions mitigation technologies.

5. Results

5.1. Experimental VLE data for the unloaded ternary AMP/PZ/H₂O system

New VLE data at 30 °C, 40 °C, and 50 °C and AMP:PZ molar ratios of 3:1.5, 4:1, and 6:1 are experimentally determined for the first time in this work, complementing the VLE data at 60 °C, 70 °C, 80 °C, 90 °C, and 100 °C, previously reported in Hartono et al., 2013. The new VLE data sets are presented in Table 4 and Fig. 1, covering a range of amine concentrations in the vapor phase from 0.0023 %vol to 0.31 %vol for AMP (corresponding to 90 to 1.2×10^4 mg/Nm³) and from 0.0003 %vol to 0.039 %vol for PZ (corresponding to 5.5 to 1.5×10^3 mg/Nm³), and a range of amine concentration in the liquid phase from 0.045 %vol to 18.64 %vol for AMP and from 0.013 %vol to 3.44 %vol for PZ.

For reference, in experimental test campaigns of CESAR1, conducted under conditions where volatile amine emissions predominate over aerosol amine emissions, concentrations of ca. 30 mg/Nm³ for AMP and ca. 9 mg/Nm³ for PZ were observed in the flue gas stream leaving the water wash. The molar fractions of AMP and PZ in the water collected from the water wash system are reported to be 0.7 %vol AMP and 0.07 %vol PZ (Moser et al., 2023). These measurements were obtained without the implementation of additional emissions mitigation measures other than the single water wash. After the application of emissions mitigation technologies, AMP and PZ emissions decreased to levels below the detection limit of the FTIR analyser, which is approximately 1 ppmv (equivalent to 3.8 mg/Nm³) (Moser et al., 2023). Real plant operation

Table 5Binary interaction parameters of AMP(1) + PZ(2) + H₂O(3) for NRTL model in Aspen Plus (Yi et al., 2024).

Parameter	Quantity	Parameter	Quantity
a ₁₃	-0.67	a ₃₁	4.10
b ₁₃	-292.22	b ₃₁	-558.33
a ₂₃	0.48	a ₃₂	7.23
b ₂₃	-1030.94	b ₃₂	-2147.71
a ₁₂	0	a ₂₁	0
b ₁₂	0	b ₂₁	0

Table 6Binary interaction parameters of AMP(1) + PZ(2) + H₂O(3) for NRTL model in Matlab (Hartono et al., 2021a).

Parameter	Quantity	Parameter	Quantity
a ₁₃	-0.34	a ₃₁	4.49
b ₁₃	-546.92	b ₃₁	-372.03
a ₂₃	-0.60	a ₃₂	5.32
b ₂₃	-598.51	b ₃₂	-1279.99
a ₁₂	88.86	a ₂₁	-1.58
b ₁₂	0	b ₂₁	0

data therefore fall in the lower end of the concentration range investigated in this work.

Experimental VLE data shows increased amine volatility at high temperatures and high amine concentrations. Increasing the AMP:PZ ratio does not appear to have a significant effect on either AMP or PZ volatility, which suggests a minimal interaction between amine molecules within the explored range of concentrations. The scatter in experimental data could be attributed to challenges in sampling at lower temperatures and total pressures. Additionally, PZ volatility is notably low. This can increase the relative errors between the model and data.

6. Volatility modeling predictions for the unloaded ternary AMP/PZ/H₂O system

The set of VLE data experimentally obtained has shown insufficient to regress the four binary interaction parameters for the AMP/PZ system within the ranges of physical validity and/or with statistical significance (i.e., low standard deviations). The newly developed NRTL/eNRTL models are therefore used to compare predicted amine volatility with experimental VLE data. Table 5 and Table 6 present the binary interaction parameters for AMP(1)/PZ(2)/H₂O(3) obtained in the regression of the NRTL/eNRTL models in Aspen Plus and Matlab respectively, where a₁₂, a₂₁, b₁₂ and b₂₁ are set to zero in Aspen Plus, and b₁₂ and b₂₁ are set to zero in Matlab model.

Experimental AMP and PZ volatility measured in this work and in Hartono et al., 2013 are compared with predicted values obtained by the newly developed NRTL/eNRTL thermodynamic models in Aspen Plus (continuous lines) (Yi et al., 2024) and Matlab (dashed lines) (Hartono et al., 2021a), in Fig. 1 and Fig. 2, respectively. Fig. 1 shows the experimental AMP and PZ volatility obtained in this work for the unloaded ternary system at 30 °C, 40 °C, and 50 °C. Fig. 2 shows the experimental AMP and PZ volatility provided in Hartono et al., 2013 for the unloaded ternary system at 60 °C, 70 °C, 80 °C, 90 °C, and 100 °C. The deviation between experimental and predicted values is more significant at low temperatures, e.g., from 30 °C to 60 °C, and low amine concentrations in the aqueous solutions for both PZ and AMP.

To extend this analysis, experimental AMP and PZ volatility measured by Li et al. (Li et al., 2013) for an unloaded solvent containing 22.3 M AMP and 5 M PZ are also compared with predicted values using the NRTL models in Fig. 3. Due to the higher concentrations, the calculated AMP and PZ partial pressures closely align with the experimental values.

The NRTL/eNRTL thermodynamic model demonstrates accurate prediction of AMP volatility, yet the PZ volatility is underpredicted at low temperatures and low concentrations. The deviation of the model results from the experimental data expressed as absolute average relative deviations (AARD) remains relatively high, approximately 44 % for

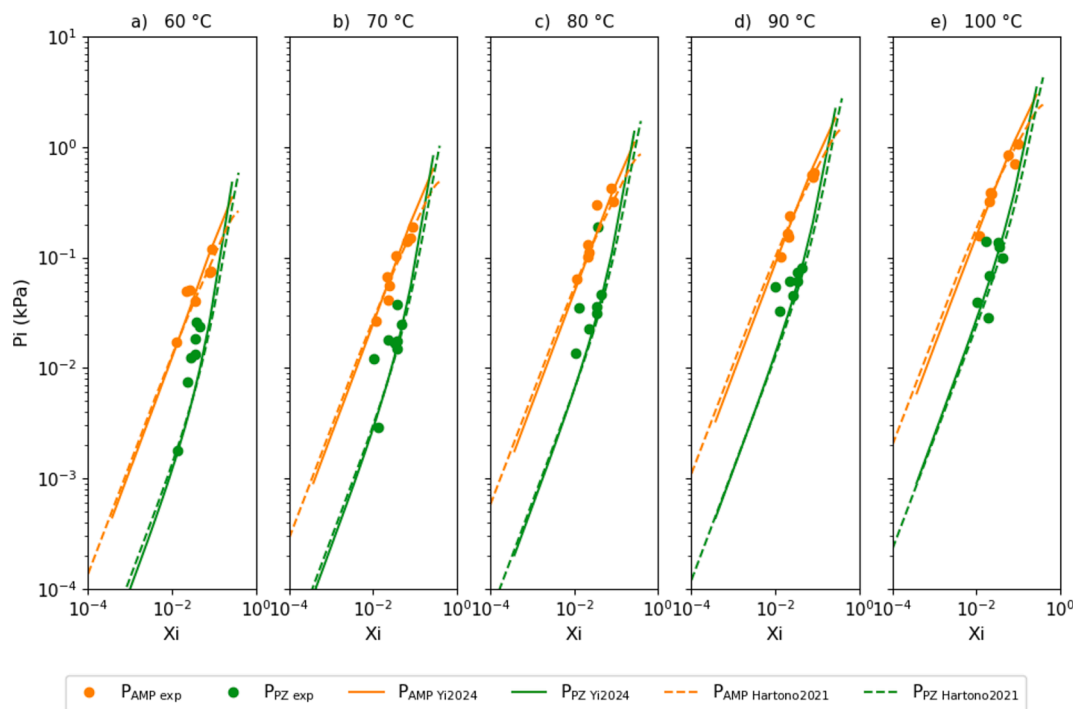


Fig. 2. Volatility of AMP and PZ and representation of the NRTL model for the unloaded AMP/PZ/H₂O system at different temperatures: (a) 60 °C, (b) 70 °C, (c) 80 °C, (d) 90 °C, and (e) 100 °C. ● Experimental data in Hartono et al., 2013. Continuous line: NRTL model in Aspen Plus (Yi et al., 2024). Dashed line: NRTL model in Matlab (Hartono et al., 2021a).

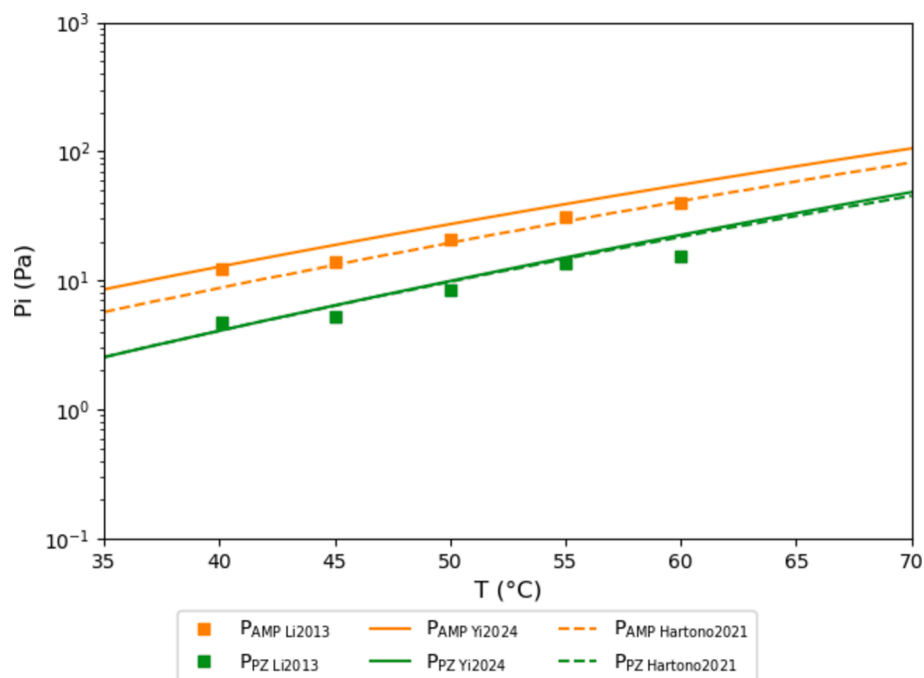


Fig. 3. Volatility of AMP and PZ and representation of the NRTL model for the unloaded AMP/PZ/H₂O system (i.e., 2.3 M AMP and 5 M PZ) as a function of temperature. Continuous line: NRTL model in Aspen Plus (Yi et al., 2024). Dashed line: NRTL model in Matlab (Hartono et al., 2021a). Experimental data in Li et al., 2013.

AMP partial pressure and 64 % for PZ partial pressure, due to the scatter in experimental data. However, these deviations are somewhat smaller compared to the experimental VLE data at higher temperatures, with AARD values of about 18 % for AMP partial pressure and 40 % for PZ partial pressure (Hartono et al., 2013).

7. Conclusions

New VLE ebulliometric data are experimentally determined for the first time in this work for aqueous solutions of AMP/PZ blends for a range of temperatures (i.e., 30 °C, 40 °C, and 50 °C) and AMP:PZ ratios (i.e., 3:1.5, 4:1, and 6:1), covering a range of amine concentrations in vapor phase from 90 to 1.2×10^4 mg/Nm³ for AMP and from 5.5 to 1.5×10^3 mg/Nm³ for PZ. These concentrations represent typical operating conditions encountered in water wash systems located at the top of absorber columns for emissions control in amine-based carbon capture systems.

Experimental results demonstrated that AMP exhibits significantly higher volatility than PZ, and determining PZ concentrations in the vapor phase have posed significant challenges, particularly at low temperatures, evident from the more scattered VLE data for PZ compared to AMP. The scatter in experimental data for AMP and PZ vapor phase concentration may be attributed to challenges in obtaining VLE data at low temperatures and low amine concentrations reducing the amount of amine in the gas phase. No notable impact on the volatility of either AMP or PZ is observed with an increase in the AMP:PZ ratio within the range of amine concentrations investigated in this study, which may suggest a weak interaction between amine molecules.

Newly developed NRTL/eNRTL thermodynamic models in Aspen Plus (Yi et al., 2024) and Matlab (Hartono et al., 2021a) for the quaternary AMP/PZ/CO₂/H₂O system exhibit a good correlation with experimental data for AMP and underpredicts PZ volatility over a broad temperature range and various AMP:PZ ratios. The deviation of the model predicted values from the experimental data expressed as AARD is approximately 44 % for AMP partial pressure and 64 % for PZ partial pressure, due to the scatter in experimental data. However, these deviations are somewhat smaller at higher temperatures, with AARD

values of about 18 % for AMP partial pressure and 40 % for PZ partial pressure. Subsequent efforts will be directed towards validating a rate-base process model using pilot plant data, with a specific emphasis on volatile amine emissions.

CRedit authorship contribution statement

Charithea Charalambous: Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization, Writing - review & editing, Project administration. **Laura Herraiz:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Conceptualization. **Ardi Hartono:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Hanna K. Knuutila:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Visualization. **Susana Garcia:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to acknowledge the financial support of the UK CCS Research Centre (www.ukccsrc.ac.uk) in carrying out this work. The UKCCSRC is funded by the EPSRC as part of the UKRI Energy Programme. The authors would like to extend their gratitude to the finalized ACT ALIGN-CCUS Project (No 271501), the follow up ACT SCOPE Project (No 691712), to the Research Centre for Carbon Solutions (RCCS) at Heriot-Watt University and the absorption laboratories of the Norwegian University of Science and Technology (NTNU) for the additional financial support. ACT ALIGN-CCUS project received funding

from RVO (NL), FZJ/PtJ (DE), Gassnova (NO), UEFISCDI (RO), BEIS (UK) and was co-funded by the European Commission under the Horizon 2020 programme ACT, Grant Agreement No 271501; www.alignccus.eu. ACT SCOPE project received funding from the Research Council of Norway (NO), RVO (NL), BEIS (UK), FZJ/PtJ (DE), DoE (USA) and Department of Science and Technology (India) and is cofunded by the European Commission under the Horizon 2020 programme ACT, Grant Agreement No 691712; www.scope-act.org.

Data availability

Data will be made available on request.

References

- Artanto, Yuli, James Jansen, Pauline Pearson, Graeme Puxty, Aaron Cottrell, Erik Meuleman, and Paul Feron (2014). "Pilot-scale evaluation of AMP/PZ to capture CO₂ from flue gas of an Australian brown coal-fired power station". In: *International Journal of Greenhouse Gas Control* 20, pp. 189–195. issn: 1750-5836. doi: <https://doi.org/10.1016/j.ijggc.2013.11.002>. url: .
- Herbert I. Britt and Richard H. Luecke (1973). "The Estimation of Parameters in Nonlinear, Implicit Models". In: *Technometrics* 15, pp. 233–247. url: <https://api.semanticscholar.org/CorpusID:121001953>.
- Brüder, Peter, Andreas Grimstvedt, Thor Mejdell, and Hallvard Svendsen (2011). "CO₂ capture into aqueous solutions of piperazine activated 2-amino-2-methyl-1-propanol". In: *Chemical Engineering Science* 66, pp. 6193–6198. issn: 1750-5836. doi: [10.1016/j.ces.2011.08.051](https://doi.org/10.1016/j.ces.2011.08.051).
- Eirik F. da Silva, Hélène Lepaumier, Andreas Grimstvedt, Solrun Johanne Vevelstad, Aslak Einbu, Kai Vernstad, Hallvard F. Svendsen, and Kolbjørn Zahlens (2012). *Industrial & Engineering Chemistry Research* 51 (41), 13329–13338. DOI: [10.1021/ie300718a](https://doi.org/10.1021/ie300718a).
- Dash, Sukanta Kumar, Amar Nath Samanta, and Syamalendu S. Bandyopadhyay (2011). "Solubility of carbon dioxide in aqueous solution of 2-amino-2-methyl-1-propanol and piperazine". In: *Fluid Phase Equilibria* 307, pp. 166–174. issn: 0378-3812. doi: [10.1016/j.fluid.2011.05.009](https://doi.org/10.1016/j.fluid.2011.05.009).
- DIPPR-801 (2004). "The information and data evaluation manager for design institute for physical properties". In: *Version 4.1.0.*
- Feron, Paul H.M., Ashleigh Cousins, Kaiqi Jiang, Rongrong Zhai, and Monica Garcia (2020). "An update of the benchmark post-combustion CO₂-capture technology". In: *Fuel* 273, p. 117776. issn: 0016-2361. doi: [10.1016/j.fuel.2020.117776](https://doi.org/10.1016/j.fuel.2020.117776).
- Hartono, A., Ahmad, R., Usman, M., Asif, N., Svendsen, H.F., 2020. Solubility of CO₂ in 0.1M, 1M and 3M of 2-amino-2-methyl-1-propanol (AMP) from 313 to 393K and model representation using the eNRTL framework. *Fluid Phase Equilibria* 511. <https://doi.org/10.1016/j.fluid.2020.112485>.
- Hartono, A., Ahmad, R., Svendsen, H.F., Knuutila, H.K., 2021a. New solubility and heat of absorption data for CO₂ in blends of 2-amino-2-methyl-1-propanol (AMP) and Piperazine (PZ) and a new eNRTL model representation. *Fluid Phase Equilibria* 550. <https://doi.org/10.1016/j.fluid.2021.113235>.
- Hartono, Ardi, Muhammad Saeed, Arlinda F. Ciftja, and Hallvard F. Svendsen (2013). "Binary and ternary VLE of the 2-amino-2-methyl-1-propanol (AMP)/piperazine (Pz)/water system". In: *Chemical Engineering Science* 91, pp. 151–161. issn: 00092509. doi: [10.1016/j.ces.2013.01.015](https://doi.org/10.1016/j.ces.2013.01.015).
- Hartono, A., Rafiq, A., Gondal, S., Svendsen, H.F., 2021b. Solubility data for Nitrous Oxide (N₂O) and Carbon dioxide (CO₂) in Piperazine (PZ) and a new eNRTL model. *Fluid Phase Equilibria* 538. <https://doi.org/10.1016/j.fluid.2021.112992>.
- Kim, Inna, Hallvard F. Svendsen, and Eli Børresen (2008). "Ebulliometric Determination of Vapor-Liquid Equilibria for Pure Water, Monoethanolamine, N-Methyl-diethanolamine, 3-(Methylamino)-propylamine, and Their Binary and Ternary Solutions". In: *J. Chem. Eng. Data* 53, pp. 2521–2531. issn: 1520-5134. doi: [10.1021/jc800290k](https://doi.org/10.1021/jc800290k).
- Kim, Inna, Erik T. Hessen, Tore Haug-Warberg, and Hallvard F. Svendsen (2009). "Enthalpies of absorption of CO₂ in aqueous alkanolamine solutions from e-NRTL model". In: *Energy Procedia* 1, pp. 829–835. issn: 18766102. doi: [10.1016/j.egypro.2009.01.110](https://doi.org/10.1016/j.egypro.2009.01.110).
- Li, Han, Le Li, Thu Nguyen, Gary T. Rochelle, and Jian Chen (2013). "Characterization of Piperazine/2-Aminomethylpropanol for Carbon Dioxide Capture". In: *Energy Procedia* 37, pp. 340–352. issn: 1876-6102. doi: [10.1016/j.egypro.2013.05.120](https://doi.org/10.1016/j.egypro.2013.05.120).
- Li, Han, Peter T. Frailie, Gary T. Rochelle, and Jian Chen (2014). "Thermodynamic modeling of piperazine/2-aminomethylpropanol/CO₂/water". In: *Chemical Engineering Science* 117, pp. 331–341. issn: 00092509. doi: [10.1016/j.ces.2014.06.026](https://doi.org/10.1016/j.ces.2014.06.026).
- Maxime H. J.-J. François, Dhruva Patil, Samuel Brulé, and Hanna K. Knuutila (2024). "CO₂ solubility and amine volatility data for low-concentration solutions of MEA, AMP, PZ and CESAR-1 blend (AMP/PZ)". In: *Results in Engineering* 22, p. 102163. issn: 2590-1230. <https://doi.org/10.1016/j.rineng.2024.102163>.
- Moser, Peter, Sandra Schmidt, Knut Stahl, Gerald Vorberg, Gustavo A. Lozano, Torsten Stoffregen, and Frank Rosler (2014). "Demonstrating Emission Reduction – Results from the Postcombustion Capture Pilot Plant at Niederaussem". In: *Energy Procedia* 63. 12th International Conference on Greenhouse Gas Control Technologies, GHGT-12, pp. 902–910. issn: 18766102. doi: <https://doi.org/10.1016/j.egypro.2014.11.100>. url: <https://www.sciencedirect.com/science/article/pii/S1876610214019158>.
- Moser, Peter, Georg Wiechers, Sandra Schmidt, Juliana Garcia Moretz Sohn Monteiro, Earl Goetheer, Charithea Charalambous, Susana Garcia, and Eva Sanchez Fernandez (2020). "ALIGN-CCUS: 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". In: *International Journal of Greenhouse Gas Control* 95. issn: 1750-5836. doi: [10.1016/j.ijggc.2019.102945](https://doi.org/10.1016/j.ijggc.2019.102945).
- Moser, Peter, Georg Wiechers, Sandra Schmidt, Juliana Garcia Moretz Sohn Monteiro, Earl Goetheer, Charithea Charalambous, Ahmed Saleh, Mijndert van der Spek, and Susana Garcia (2021). "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". In: *International Journal of Greenhouse Gas Control* 109. issn: 17505836. doi: [10.1016/j.ijggc.2021.103381](https://doi.org/10.1016/j.ijggc.2021.103381).
- Moser, Peter, Georg Wiechers, Marcel Busch, Knut Stahl, Susana Garcia, Laura Herraiz, Charithea Charalambous, Mijndert van der Spek, Hallvard F. Svendsen, Maxime Francois, Hanna K. Knuutila, Peter van Os, Juliana Garcia Moretz-Sohn Monteiro, Roberta Veronezi Figueiredo, and Eirini Skylogianni (2023). "SCOPE - Volatile and aerosol-based emissions of aged CESAR1 and their mitigation - measurement and simulation". In: *TCCS-12, June 2023, Trondheim, Norway*.
- Prausnitz, J.H., Lichtenthaler, R.N., de Azevedo, E.G., 1998. *Molecular thermodynamics of fluid-phase equilibria*. Pearson Education.
- Rieder, Alexander, Sanjana Dhingra, Purvil Khakharia, Luigi Zangrilli, Bernd Schallert, Robin Irons, Sven Unterberger, Peter Os, and Earl Goetheer (2017). "Understanding Solvent Degradation: A Study from Three Different Pilot Plants within the OCTAVIUS Project". In: *Energy Procedia* 114, pp. 1195–1209. doi: .
- Spietz, T., Chwola, T., Krótki, A., et al., 2018. Ammonia emission from CO₂ capture pilot plant using aminoethylethanolamine. *Int. J. Environ. Sci. Technol.* 15, 1085–1092. <https://doi.org/10.1007/s13762-017-1475-z>.
- Tong, Danlu, Geoffrey C. Maitland, Martin J.P. Trusler, and Paul S. Fennell (2013). "Solubility of carbon dioxide in aqueous blends of 2-amino-2-methyl-1-propanol and piperazine". In: *Chemical Engineering Science* 101, pp. 851–864. issn: 0009-2509. doi: [10.1016/j.ces.2013.05.034](https://doi.org/10.1016/j.ces.2013.05.034).
- Spek, Mijndert van der, Richard Arendsen, Andrea Ramirez, and Andfe Faaij (2016). "Model development and process simulation of postcombustion carbon capture technology with aqueous AMP/PZ solvent". In: *International Journal of Greenhouse Gas Control* 47, pp. 176–199. issn: 1750-5836. doi: .
- Vevelstad, Solrun Johanne, Andreas Grimstvedt, Jørund Elnan, Eirik Falck da Silva, and Hallvard F. Svendsen (2013). "Oxidative degradation of 2-ethanolamine: The effect of oxygen concentration and temperature on product formation". In: *International Journal of Greenhouse Gas Control* 18, pp. 88–100. issn: 1750-5836. doi: [10.1016/j.ijggc.2013.06.008](https://doi.org/10.1016/j.ijggc.2013.06.008).
- Wanderley, Ricardo R., Diego D.D. Pinto, and Hanna K. Knuutila (2020). "Investigating opportunities for water-lean solvents in CO₂ capture: VLE and heat of absorption in water-lean solvents containing MEA". In: *Separation and Purification Technology* 231. issn: 18733794. doi: [10.1016/j.seppur.2019.115883](https://doi.org/10.1016/j.seppur.2019.115883).
- Weir, Henry, Eva Sanchez-Fernandez, Charithea Charalambous, Jasper Ros, Juliana Garcia MoretzSohn Monteiro, Eirini Skylogianni, Georg Wiechers, Peter Moser, Mijndert van der Spek, and Susana Garcia (2023). "Impact of high capture rates and solvent and emission management strategies on the costs of full-scale post-combustion CO₂ capture plants using long-term pilot plant data". In: *International Journal of Greenhouse Gas Control* 126, p. 103914. issn: 17505836. doi: [10.1016/j.ijggc.2023.103914](https://doi.org/10.1016/j.ijggc.2023.103914).
- Yi, Ningtong, Laura Herraiz, Mengxiang Fang, Susana Garcia, and Mijndert van der Spek (2024). "Open access, thermodynamically consistent, electrolyte NRTL model for piperazine, AMP, water, CO₂ systems on Aspen Plus". In: *Separation and Purification Technology*, Submitted.