

Characterization of 2-Piperidineethanol and 1-(2-Hydroxyethyl)pyrrolidine as strong bicarbonate forming solvents for CO₂ capture

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Highlights

- CO₂ solubility in aqueous solutions of 50 mass% 2-Piperidineethanol (2-PPE) and 40 mass% 1-(2-Hydroxyethyl)pyrrolidine (1-(2HE)PRLD) were measured at 40-120°C
- Density and viscosity were measured at 20-80°C and fitted to a simplified correlation as functions of loading and temperature
- Thermal degradation tests show that both solvents are more stable and less corrosive than 30 mass% MEA

- The oxidative degradation rate of 1-(2HE)PRLD is lower than that of 30 mass% MEA while 2-PPE degrades much faster
- Environmental properties tests have shown that both amines are not toxic and readily biodegradable

Abstract

The solubility of CO₂ in the aqueous solutions of 50 mass% 2-Piperidineethanol (2-PPE) and 40 mass% 1-(2-Hydroxyethyl)pyrrolidine (1-(2HE)PRLD) was measured at temperatures from 40 to 120°C at CO₂ loading from 0.04 to 0.8 mol-CO₂/mol-amine. The density and viscosity of unloaded and CO₂-loaded solutions were measured at temperatures between 20 and 80°C and fitted to simplified correlations. Based on a thermal degradation test, both solvents were found to be more stable and less corrosive than 30 mass% MEA. However, oxidative degradation tests indicate that the 1-(2HE)PRLD degradation rate is lower than that of 30 mass% MEA while 2-PPE degrades much faster. From the environmental aspect, both solvents are found to be non-toxic and biodegradable in fresh water. These experimental data will be used for estimation of the energetic and environmental potential as solvents for CO₂ capture.

1. Introduction

CO₂ capture aims to separate CO₂ from the inlet stream and produce more concentrated CO₂ that can be readily transported to a CO₂ storage site. New or improved methods of CO₂ capture, combined with advanced power systems and industrial process designs, can significantly reduce CO₂ capture costs, energy requirements and minimize the overall environmental impacts (Edenhofer, 2014)

Alkanolamines are widely used as solvents for post-combustion CO₂ capture because the compounds have two functional groups which in combination give an increase in CO₂ solubility in water and thus higher absorption of CO₂ (Kohl and Nielsen, 1997). Alkanolamines react with CO₂ and form bicarbonate and carbamate:



Reaction R₁ represents the bicarbonate formation and if any system produces mainly bicarbonate, then the loading capacity is close to unity but the absorption rate is usually slow. The reaction R₂ represents the carbamate formation typical for primary and secondary amines. The absorption capacity of the carbamate forming solvents having single amine functionality is limited to 0.5 mol-CO₂/mol-amine but the absorption rate is usually higher than that of the reaction R₁. The ratio between bicarbonate and carbamate formation, depending on the properties of the amine and on process conditions. In the concept of *strong bicarbonate former* mainly reaction (1) takes place. A solution with a higher bicarbonate to carbamate ratio is expected to have high absorption capacity for CO₂ and give a leaner solution upon regeneration (Sartori and Savage, 1983).

In our previous work (Hartono et al., 2017), fifteen strong bicarbonate forming amines were investigated in a screening apparatus and the pKa (dissociation constant) were measured at 25°C. Two solvents, 50 mass% 2-PPE and 40 mass% 1-2(HE)PRLD) were selected for further studies.

2-Piperidineethanol is a sterically hindered secondary amine, studied as promising solvent for CO₂ capture by several researchers due to its potential as it has high cyclic capacity and fast absorption rates at high CO₂ loadings (Sartori and Savage, 1983). Different works have reported the physical properties of unloaded solvent (density, viscosity and N₂O solubility) at different

temperatures and amine concentrations (Aguila-Hernández et al., 2001; Paul and Mandal, 2006; Xu et al., 1992), heat capacity (Chiu and Li, 1999), heat of absorption (Chowdhury et al., 2013b), CO₂ reaction kinetics (Chen and Rochelle, 2011; Paul et al., 2009; Shen et al., 1991; Xu et al., 1993), dissociation constant (Fernandes et al., 2012; Hartono et al., 2017; Xu et al., 1992) and CO₂ solubility (Chen and Rochelle, 2011). Also, a rigorous thermodynamic model (electrolyte-NRTL) and activity-based kinetics with NMR results (Sherman et al., 2016) have been published.

1-(2-Hydroxyethyl)pyrrolidine is a tertiary amine reported by Chowdhury, et al. (Chowdhury et al., 2013a) to have good potential as a solvent candidate for CO₂ capture due to a moderate absorption rate, high absorption capacity and low absorption heat (-58 kJ/ mole CO₂). Liu, et al. (Liu et al., 2016; Liu et al., 2017) also recently reported kinetic data from a stop flow apparatus, dissociation constants up to 45°C, CO₂ solubility into 2M solution at two temperatures (25 and 40°C) and at CO₂ partial pressures between 8-101kPa.

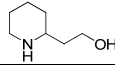

The objective of this work is to estimate the environmental properties of the selected amines and produce experimental data necessary for the evaluation of the energetic potential of these two amines in post-combustion CO₂ capture. Vapor-liquid equilibrium (VLE) measurements have been done at temperatures between 40 and 120°C and loadings between 0.04 and 0.8 mol-CO₂/mol-amine. The viscosity and density of both solvents have been measured for unloaded and CO₂-loaded solutions between 20 and 80°C. Furthermore, thermal and oxidative degradation tests have been performed, and the environmental properties (eco-toxicity and bio-degradability) of the amines have been evaluated.

2. Experimental

2.1. Chemicals

The chemicals used in this work (Table 1) were used as received without any further purification. Aqueous solutions of 2-PPE and 1-(2HE)PRLD were prepared gravimetrically using distilled de-ionized water. 30 mass% solutions of both of them were used for oxidative and thermal degradation experiments. For all other experiments 50 mass% 2-PPE and 40 mass% 1-(2HE)PRLD were used.

Table 1. Chemicals used in this work

NO.	Chemical Name	Abbreviation	CAS No.	Structure	M (g/mol)	Supplier*	Purity (%min)
1	2-Piperidineethanol	2-PPE	1484-84-0		129.20	TCI AO	96 95
2	1-(2-Hydroxyethyl)pyrrolidine	1-(2HE)PRLD	2955-88-6		115.17	SA AA	97 97
3	Carbon Dioxide	CO ₂	124-38-9	CO ₂	44.01	AGA	99.999
4	Nitrogen	N ₂	7727-37-9	N ₂	28.02	AGA	99.998

*AA=Alfa Aesar AO=Acros Organics SA=Sigma Aldrich TCI=Tokyo Chemical Industry

2.2. Experimental

2.2.1. Vapor-liquid equilibrium measurements

Vapor-liquid equilibrium (VLE) was measured using two setups.

Atmospheric pressure (low-temperature) VLE apparatus

The atmospheric pressure VLE apparatus described in detail by (Ma'mun et al., 2006) was used in this work for measurements at temperatures between 40 and 80°C (Figure 1). The apparatus consists of four 360 ml glass flasks immersed in a water bath and placed in a heating cabinet, a BÜHLER gas circulation pump, and an X-STREAM CO₂ Gas Analyzer (XEGK) equipped with 2 channels for CO₂ (0-1±0.1% and 0-100±0.5%). The temperatures of the solution (in flask 4), water bath and in the condenser are measured using K-type thermocouples (±0.1°C).

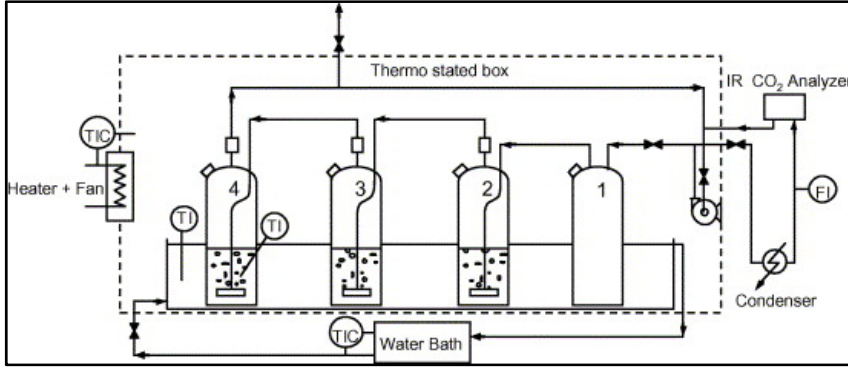


Figure 1. Atmospheric pressures VLE Apparatus (Ma'mun et al., 2006) (FI, Flow Indicator; TI, Temperature Indicator; TIC, Temperature Indicator and Control)

For the equilibrium measurements, about 150 ml of a preloaded amine solution was fed into each of flasks 2, 3 and 4, while flask 1 remained empty to stabilize the gas flow. The solution and thermostated box were heated to the desired temperature. When the temperature was reached, the gas phase was circulated using the gas pump and the CO₂ concentration in the gas phase was measured by a CO₂ analyzer. The system was assumed to be at equilibrium when the CO₂ concentration in the gas phase was constant for at least 30 min. At equilibrium, the concentration of the CO₂ in the gas phase was recorded and liquid sample was withdrawn from flask 4 and analyzed for amine and CO₂ as described by Ma'mun et al. (Ma'mun et al., 2006). The procedure was repeated with the solutions with different CO₂ loadings. Both the amine and CO₂ analyses are estimated to have uncertainty of less than 2%.

The partial pressure of CO₂ (P_{CO_2}) was calculated according to (Aronu et al., 2011):

$$P_{CO_2} (kPa) = y_{CO_2} \cdot (P_{amb} - P_{Solvent}^{T_{Exp}} + P_{Solvent}^{T_{Cond}}) \quad (1)$$

where (y_{CO_2}) is CO₂ concentration measured by CO₂ analyzer (vol.%), (P_{amb}) is ambient pressure, $P_{Solvent}^{T_{Exp}}$ is the vapor pressure of the solvent at the required experimental temperature, $P_{Solvent}^{T_{Cond}}$ is the vapor pressure of solvent at the outlet of the condenser, ($T_{Solvent}^{Exp}$) is the liquid

temperature in flask 4, and ($T_{Solvent}^{Cond}$) is the temperature of the gas entering the CO₂ analyzer (condenser temperature).

The vapor pressure of the unloaded solvent, $P_{Solvent}^T$, was measured in the medium pressure VLE apparatus presented next.

Medium pressure (high temperature) VLE apparatus

The medium pressure VLE apparatus (Figure 2) consists of Type 1B of a jacketed Büchi glass reactor with a total volume $V_R = (1100.5 \pm 0.6) \cdot 10^{-6} \text{ m}^3$ equipped with a mechanical stirrer, two Pt-100 temperature sensors for liquid and gas phase temperature measurements ($T_L(T_G) \pm 0.02^\circ\text{C}$), and three pressure transducers for accurate pressure measurements: PTX5072 (0-600±0.3 kPa), PTX517 (0-200±0.2 kPa) and PTX5022 (0-10±0.01 kPa). The glass reactor can operate up to 600 kPa and 200°C. CO₂ is added to the reactor batchwise from a SS-316 gas tank ($V_V = (1158.2 \pm 0.6) \cdot 10^{-6} \text{ m}^3$) equipped with a Pt-100 temperature sensor and PTX 610 pressure transducer (0-600±0.6 kPa). The temperature in the reactor is adjusted using a Julabo ME6 heat circulator using ethylene glycol as a heating medium. The reactor lid is heated using two silicon-heating tapes. All operation parameters are logged-on using a Lab-view program via National Instrument NI-4903 module data monitors.

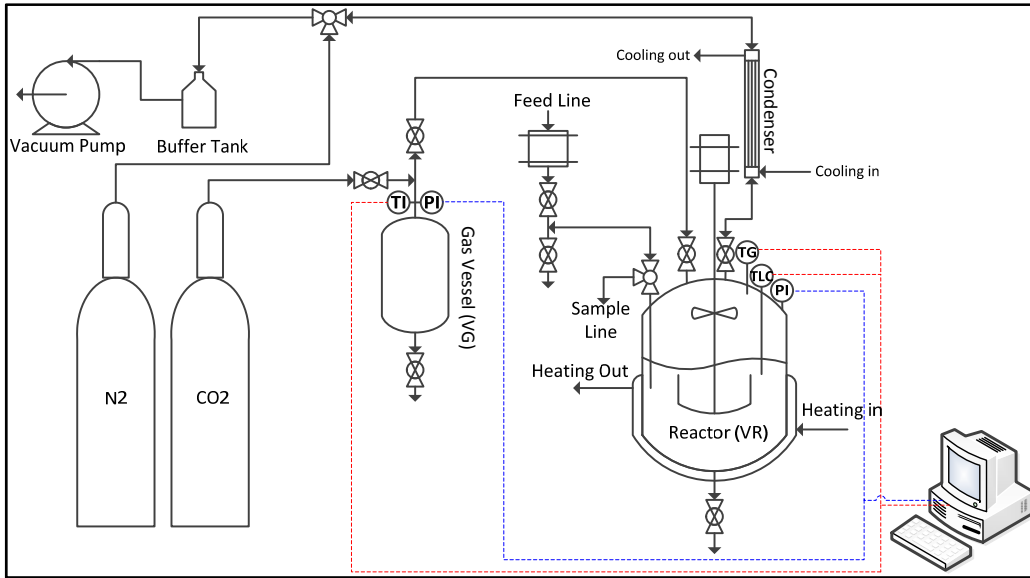


Figure 2. Medium pressure VLE apparatus (TI, Temperature Indicator; PI, Pressure Indicator)

The experiments were performed in this apparatus at temperatures between 80 and 120°C. A few data points were also measured at 60°C at high CO₂ loadings (high partial pressure of CO₂). For equilibrium measurements, about 500 ml of unloaded solution was charged into the reactor, which was previously evacuated down to ~0.2 kPa using a rotary vane pump (Pfeiffer DUO5MC). The weight of the solution added to the reactor (m_S) was noted. The solution in the reactor was evacuated for a short time to remove any dissolved gas in the solution, then the desired temperature was set and the system was left to reach equilibrium. Equilibrium was assumed to be reached when gas and liquid temperatures (T_G and T_L) and pressure (P_R) in the reactor were constant for at least 15 minutes. For equilibrium measurements for loaded solutions, CO₂ was added to the reactor from the CO₂ gas tank in several steps.

The partial pressure of CO₂ in the reactor was calculated from the total pressure measurements (P_R) assuming that the partial pressure of the solvent (P_S) remained constant during isothermal experiment (Hartono et al., 2008):

$$P_{CO_2} (kPa) \cong P_R - P_S \quad (2)$$

The amount of CO₂ added to the reactor was calculated from the pressure drop in the CO₂ tank using Peng-Robinson equation of state (Peng and Robinson, 1976):

$$n_{CO_2}^{added} (mol) = \frac{V_V (m^3)}{R \left(\frac{m^3 \cdot kPa}{K \cdot mol} \right) \cdot T_V (K)} \cdot \left[\frac{P_V^{Initial} (kPa)}{Z_{Initial}} - \frac{P_V^{Final} (kPa)}{Z_{Final}} \right] \quad (3)$$

The amount of CO₂ accumulated in the reactor gas phase at each loading was estimated from:

$$n_{CO_2}^{gas\ phase} (mol) = \frac{P_{CO_2} (kPa) \cdot V_G (m^3)}{R \left(\frac{m^3 \cdot kPa}{K \cdot mol} \right) \cdot T_G (K) \cdot Z_{CO_2}} \quad (4)$$

Where the gas phase volume, V_G , is calculated as the difference between the volume of the reactor V_R and the volume of the solvent V_S at experimental temperature while V_V, T_V, Z_i and R represent gas vessel's volume, temperature, gas (CO₂) compressibility factor and universal gas constant, respectively.

The loading of solution is calculated from the amount of absorbed gas in the liquid phase:

$$\alpha (mol\ CO_2 / mol\ Amine) = (n_{CO_2}^{added} - n_{CO_2}^{gas\ phase}) / n_{amine}$$

2.2.2 Physical properties measurements

Densities of the unloaded and CO₂-loaded 2-PPE and 1-2(HE)PRLD solutions were measured using Anton Paar Density meter DMA 4500M used previously by (Hartono et al., 2014). The system can be operated at temperatures up to 90±0.01 °C, densities up to 3·10³ kg/m³ with the level of uncertainty within 0.05 kg/m³. The system was calibrated by measuring the densities of air and water at 20 °C (Hartono et al., 2014).

The viscosities of the amine solutions were measured using Anton Paar Physica MCR 100 rheometer with a double-gap measuring cell previously used by (Hartono et al., 2014). The measurements were performed at temperatures between 20 and 80(± 0.03)°C under atmospheric pressure. The standard viscosity solution (D5) from Paragon Scientific Ltd. was used for the

calibration of the instrument. The instrument measures shear stress at a controlled shear rate. The dynamic viscosity of the samples is determined from the slope between the shear rate and shear stress. The reported data points are the averages of at least two parallel measurements. The uncertainty of the experimental data, estimated from the parallel measurements, is $\pm 2\%$.

The solutions at different loadings were prepared by diluting the solution with the highest loading with the unloaded solution. The loadings of the new solutions were verified with amine and the CO₂ titration method. The uncertainty of the loading is estimated to be 3%.

2.2.3. Solvent degradation measurements and environmental properties tests

In the post-combustion process the degradation tests are usually conducted in two different experiments, each simulating a different part of the process. Thermal degradation of amine is usually determined at high temperature and CO₂ concentration (stripper conditions) while for the absorber conditions, experiments at lower temperature are performed in the presence of oxygen and CO₂ (oxidative degradation). In a real process, an overall effect will be observed due to solvent circulation. Other important properties of the solvent to be evaluated during solvent development are its environmental properties – ecotoxicity and biodegradability as well as nitrosamines formation.

Oxidative degradation

Oxidative degradation experiments were performed using the setup described by (Vevelstad et al., 2013) and shown in Figure 3, by bubbling a humidified mixture of air (0.35 l/min) and CO₂ (0.075 l/min) through an amine solution (about 0.9 l) placed in the jacketed glass reactor (1 l liquid volume). The experiments were conducted at 55°C for 3 weeks. The samples from the liquid phase were taken regularly and analyzed for water content by Karl Fisher titration, and for the specific amine component using LC-MS. In addition, the initial and the end samples were

analyzed for total amine and CO₂ concentrations. For the end sample, organic nitrogen was measured using the Kjeldahl method. Depending on amine, selected samples were in addition analyzed for ammonia, other degradation product suspected for the specific amine (i.e., pyrrolidine for 1-(2HE)PRLD) and nitrosamine (total nitrosamine or specific nitrosamine, i.e., *N*-nitrosopyrrolidine for 1-(2HE)PRLD). Ammonia, pyrrolidine and specific nitrosamine were analyzed using Liquid Chromatography – Mass Spectrometry (LC-MS). The details with regard to the column, ion source and mobile phase are given in Appendix A1 in Table A1 and more details can be found in (Vevelstad, 2013). The total Nitrosamine was analyzed using Gas Chromatography (GC) with Nitrogen Chemiluminescence Detector (NCD).

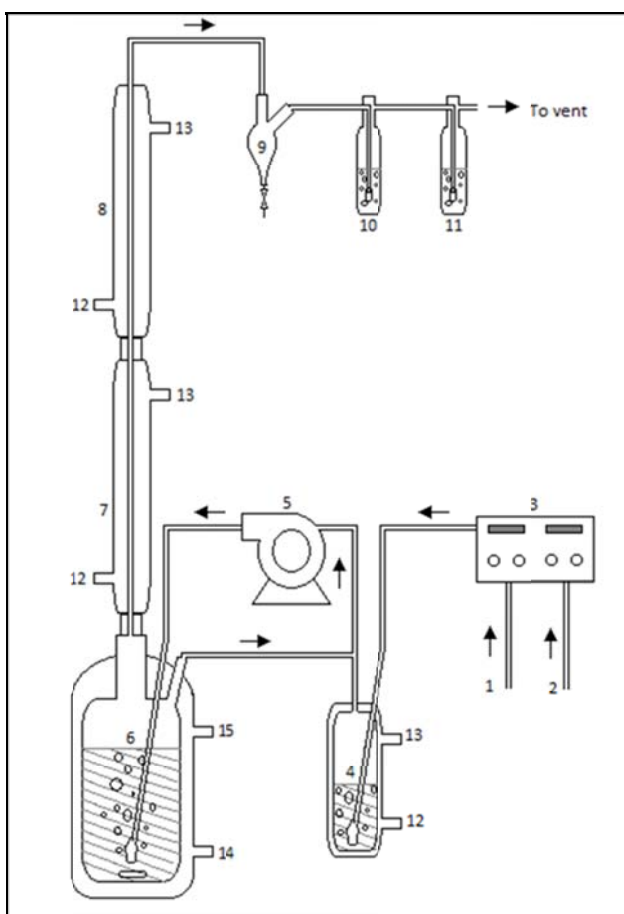


Figure 3. Schematic diagram of the oxidative degradation setup (1. CO₂; 2. Air; 3. MFC (Mass Flow Controller); 4. A jacketed water saturation vessel with a glass sinter; 5. Gas

Circulation Pump; 6. A jacketed reactor with a glass sinter; 7/8. Water condensers; 9. Separation funnel; 10/11. Acid traps (H₂SO₄ 1M); 12/13. Cooling water inlet/ outlet; 14/15. Water bath inlet/outlet).

Thermal degradation

Thermal degradation experiments were conducted as described by (Lepaumier et al., 2011) using stainless steel tube cells (316SS, OD = ½", thickness = 1.7 mm) of about 27 cm³ total volume with a Swagelok valve. A set of experiments is normally performed with 5 cells. Each cell is flushed with N₂ before adding about 15 cm³ of a CO₂-loaded amine solution. A CO₂ loaded solution was prepared gravimetrically by bubbling CO₂ through the solution. The top of the cell is flushed with N₂ before closing the valve to remove the air. The cells are then placed into a convection oven at 135°C for 5 weeks. One cell is removed each week and the content is analyzed for amine (LC-MS as described before), CO₂ using a Total in Organic Carbon (TIC)/Total Organic Carbon (TOC) analyzer (Apollo 9000 TOC Combustion Analyzer from Teledyne Tekmar Co.) and metal ions using ICP-MS (Inductively Coupled Plasma Mass Spectroscopy).

Ecotoxicity and biodegradation

Ecotoxicity tests were performed with two species representing different trophic levels in the aquatic (freshwater) food chain, the unicellular phytoplankton species *Pseudokirchneriella subcapitata* and the herbivore crustacean *Daphnia magna*. Acute toxicity was determined as the concentrations of amines, which caused 50% growth inhibition of phytoplankton or 50% immobilization of crustacean (EC₅₀), when compared to control cultures in accordance with the standard guidelines (OECD-Guideline-201, 2006; OECD-Guideline-202, 2004). In addition, concentrations resulting in 10% and 90% inhibition/immobilization (EC₁₀ and EC₉₀) were

determined. EC values with 95% confidence intervals were calculated using the software GraphPad Prism (vs. 6.0; GraphPad Software, Inc., San Diego, CA).

Biodegradability tests of the amines were performed in natural fresh surface water according to a standard closed bottle method for determining biodegradability (OECD-Guideline-301, 1992). Water from the two sources, collected from a river (Nedre Leirfoss) and a lake (Haukvatnet) close to Trondheim, Norway (63°25'N, 10°24'E), was mixed equally (total of 60 L). A part of the water (10 L) was subjected to bacterial enrichment by continuous circulation through an aquarium pump in the dark, while the rest was left without further treatment (dark). Both circulated and undisturbed water were aged at 20±2 °C for 7 days. At the end of the aging period, the accumulated bacteria in the filter of the aquarium pump were applied to the rest of the aged water and the enriched water was used as inoculum during the biodegradation testing. The water was amended with mineral solutions, as described in the guideline.

Biodegradation tests were performed in 275 ml flasks with amine concentrations of 2 mg/L at 20±2 °C for up to 28 days, while flasks with water without amines were used as blanks (OECD-Guideline-301, 1992). Sterilized controls poisoned with HgCl₂ (100 mg/L) were used to determine abiotic amine losses.

Biodegradability was determined as measured biochemical oxygen demand (BOD) compared to a theoretical oxygen demand (ThOD) describing the oxygen demand for complete biodegradation of each test substance. BOD analyses were performed in probes collected after 0, 7, 14 and 28 days of incubation. Dissolved oxygen (DO) was analyzed with a BOD probe connected to a dissolved oxygen meter (YSI, Inc., Yellow Springs, OH). BOD and the percentage biodegradability was determined as described in the guideline (OECD-Guideline-301, 1992). A reference chemical (aniline) was included and should have a biodegradability of > 60% of its ThOD value.

3. Results and Discussion

3.1. VLE measurements

The results from the low-temperature VLE measurements are summarized in Table 2 for the 50 mass% 2-PPE solution, and in Table 3 for the 40 mass% 1-(2HE)PRLD. The results from the high-temperature VLE measurements are presented in Tables 4 and 5.

The experimental data measured in this work are fitted to empirical correlations given below by minimizing of the sum of square error (SSE) according to (Weiland et al., 1993) :

$$SSE = \sum_1^N \frac{[Y_{Calc.} - Y_{Exp.}]^2}{Y_{Exp.} \cdot Y_{Calc.}} \quad (5)$$

This objective function weights all data equally, hence a systematic error in the prediction could be avoided, especially for the VLE results where the range of the data is large. Vapor pressure of the unloaded solutions (P_S) measured in this work is fitted to the Antoine equation (Antoine, 1888):

$$\ln P_S (kPa) = \left[d_1 - \frac{d_2}{d_3 + T(K)} \right] \quad (6)$$

Where d_1, d_2, d_3 are parameters fitted using VLE data for the unloaded solutions.

Partial pressure of CO₂ above the loaded solution (P_{CO_2}) is fitted to the correlation proposed by (Brüder et al., 2011).

$$\ln P_{CO_2} (kPa) = B(-) \cdot \ln(\alpha) + A_1 + \frac{C(-)}{(1 + A_2 \cdot \exp(-A_3))} \quad (7)$$

The following correlations are used in this work for the temperature dependent coefficients A_1 to A_3 :

$$A_1(-) = k_1(-) \cdot \ln\left(\frac{1}{T(K)}\right) + k_2(-) \quad (8)$$

$$A_2(-) = \exp\left(\frac{k_3(K)}{T(K)} + k_4(-)\right) \quad (9)$$

$$A_3(-) = \frac{k_5(K)}{T(K)} + k_6(-) \quad (10)$$

Where k_1, \dots, k_6 are parameters fitted using VLE data for the loaded solutions.

The Average Absolute Relative Deviation (AARD) is calculated using the following equation:

$$AARD(\%) = \frac{100}{N} \sum_1^N \left| \frac{Y_{Calc.} - Y_{Exp.}}{Y_{Exp.}} \right| \quad (11)$$

Where $Y_{Exp.}$ and $Y_{Calc.}$ are the experimental data used in the fitting and the estimated value from the model, respectively, while N is the number of data.

Parameters for the vapor pressure correlations are given in Table 6 for the unloaded solvents and in Table 7 for the CO₂-loaded solutions.

The experimental data and model predictions for the loaded solutions are compared in Figure 4a for the 2-PPE solution and in Figure 4b for the 1-(2HE)PRLD solution. It should be noted that for the 1-(2HE)PRLD solution the data points at loadings below 0.01 were not used in regression. As seen from Tables 6 and 7, the models are able to represent the data very well, with AARD of 15 and 18% for 2-PPE and 1-(2HE)PRLD solutions, respectively. Literature data for 2-PPE from (Chen and Rochelle, 2011) (symbol '+' at 40, 60, 80 and 100°C) in Figure 4a agree very well with the data from this work.

Table 2. CO₂ solubility in aqueous solution of 50 mass% 2-PPE at 40, 60 and 80°C

40°C		60°C		80°C	
α	P_{CO_2}	α	P_{CO_2}	α	P_{CO_2}
$\frac{mol\ CO_2}{mol\ Amine}$	kPa	$\frac{mol\ CO_2}{mol\ Amine}$	kPa	$\frac{mol\ CO_2}{mol\ Amine}$	kPa
0.78	10.12	0.80	58.70	0.55	55.30
0.76	8.16	0.69	33.50	0.47	34.16
0.72	5.97	0.62	18.17	0.37	17.95
0.66	3.80	0.53	9.36	0.30	11.24
0.56	2.53	0.44	5.55	0.22	6.42
0.52	1.66	0.39	3.48	0.157	3.52
0.42	0.869	0.30	1.91	0.114	2.15
0.37	0.559	0.22	0.965	0.074	1.12
0.33	0.365	0.148	0.505	0.040	0.569
0.27	0.177	0.109	0.254	0.021	0.284
0.20	0.127	0.067	0.128	0.017	0.164
0.132	0.059	0.042	0.066	0.013	0.096
0.075	0.024	0.035	0.036	0.010	0.071
0.031	0.008	-	-	0.009	0.046
0.97*	40.53	0.74*	32.63	0.39*	20.70
0.67*	5.00	0.49*	7.48	0.35*	15.49
0.42*	0.977	0.26*	1.51	0.25*	8.12

* Repetition

Table 3. CO₂ solubility in aqueous solution of 40 mass% 1-(2HE)PRLD at 40, 60 and 80°C

40°C		60°C		80°C	
α	P_{CO_2}	α	P_{CO_2}	α	P_{CO_2}
$\frac{mol\ CO_2}{mol\ Amine}$	kPa	$\frac{mol\ CO_2}{mol\ Amine}$	kPa	$\frac{mol\ CO_2}{mol\ Amine}$	kPa
0.81	29.99	0.59	26.61	0.45	48.12
0.67	10.27	0.51	18.69	0.31	31.62
0.61	6.72	0.43	13.09	0.23	24.10
0.51	4.09	0.35	8.83	0.18	13.52
0.43	2.56	0.24	4.94	0.138	9.08
0.34	1.59	0.136	2.02	0.107	5.59
0.25	0.940	0.072	0.815	0.064	3.07
0.17	0.518	0.032	0.323	0.043	1.27
0.115	0.272	0.016	0.150	0.023	0.587
0.076	0.143	0.0108	0.067	0.0123	0.188
0.046	0.069	0.004*	0.034	0.007*	0.070
0.025	0.028	-	-	0.005*	0.027
0.55**	4.82	0.59**	28.01	0.38**	52.49
0.31**	1.49	0.35**	9.81	0.18**	19.74
0.22**	0.859	0.20**	4.05	0.126**	7.81

* Close to the precision limit

** Repetition

Table 4. Total pressure(P_R), estimated CO₂ partial pressure (P_{CO_2}) and loading (α) in aqueous solution of 50% mass of 2-PPE at 80, 100 and 120°C.

80°C			100°C			120°C		
α	P_R	P_{CO_2}	α	P_R	P_{CO_2}	α	P_R	P_{CO_2}
$\frac{\text{mol } CO_2}{\text{mol Amine}}$	kPa	kPa	$\frac{\text{mol } CO_2}{\text{mol Amine}}$	kPa	kPa	$\frac{\text{mol } CO_2}{\text{mol Amine}}$	kPa	kPa
0.09	47.5	2.8	0.09	99.3	1.9	0.06	201.2	8.5
0.19	50.7	5.9	0.18	106.6	9.3	0.12	219.3	27.5
0.28	54.6	9.9	0.26	118.9	21.6	0.18	242.6	50.5
0.36	59.4	14.7	0.34	135.7	38.4	0.23	264.0	72.0
0.38	61.2	16.5	0.41	161.1	63.8	0.27	298.4	106.3
0.46	71.0	26.3	0.48	189.1	91.8	0.31	324.3	131.8
0.54	84.4	39.7	0.54	232.1	134.7	0.35	350.1	158.0
0.59	96.4	51.7	0.60	274.2	176.9	0.38	380.2	188.0
0.66	124.0	79.4	0.64	316.0	218.7	0.40	406.5	214.5
0.72	158.6	113.9	0.67	361.2	263.8	0.43	433.9	241.9
0.77	213.6	168.9	0.70	406.8	309.5	0.44	459.7	267.7
0.82	282.5	237.8	0.72	445.0	347.6	0.46	476.3	284.2
0.85	358.1	313.4	0.73	470.8	373.5	0.48	499.0	306.9
0.87	429.0	384.3	0.75	498.9	401.6	0.49	517.1	324.9
0.88	482.7	438.0	0.76	519.9	422.6	0.50	534.1	342.1
0.89	522.4	477.8	0.76	539.6	442.2	0.51	544.4	352.3

Table 5. Total pressure (P_R), estimated CO₂ partial pressure (P_{CO_2}) and loading (α) in aqueous solution of 40 mass% 1-(2HE)PRLD at 60, 80, 100 and 120°C.

120°C			100°C			80°C			60°C		
α	P_R	P_{CO_2}	α	P_R	P_{CO_2}	α	P_R	P_{CO_2}	α	P_R	P_{CO_2}
$\frac{mol\ CO_2}{mol\ Amine}$	kPa	kPa	$\frac{mol\ CO_2}{mol\ Amine}$	kPa	kPa	$\frac{mol\ CO_2}{mol\ Amine}$	kPa	kPa	$\frac{mol\ CO_2}{mol\ Amine}$	kPa	kPa
0.06	224.0	27.9	0.40	262.4	164.9	0.72	277.9	233.1	0.87	398.2	379.4
0.13	270.5	73.9	0.47	308.3	210.8	0.77	355.1	310.3	0.91	484.6	465.8
0.18	320.0	123.7	0.52	353.3	255.7	0.80	439.9	395.0	0.96	541.0	522.2
0.23	373.0	177.1	0.56	399.8	302.2	0.82	495.1	450.3	-	-	-
0.26	411.5	215.4	0.59	441.0	343.5	0.84	540.6	495.8	-	-	-
0.28	448.3	252.3	0.62	472.9	375.5	-	-	-	-	-	-
0.31	482.5	286.6	0.64	502.8	405.3	-	-	-	-	-	-
0.33	510.3	314.4	0.65	528.9	431.3	-	-	-	-	-	-

Table 6. Parameters for the vapor pressure correlation of unloaded solvents using eq. (6)

Parameter	2-PPE	1-(2HE)PRLD
d_1	19.59	18.55
d_2	6206.61	5305.77
d_3	39.91	6.53
SSE	0.001	0.003
$AARD$ (%)	0.7	1.3

Table 7. Parameters for the CO₂ Solubility correlation (eqs. 7-10)

Parameter	2-PPE	1-(2HE)PRLD
B	1.37	1.49
C	10	10
k_1	-26.78	-23.12
k_2	-153.71	-130.59
k_3	-1023.43	-1548.19
k_4	3.69	4.92
k_5	149.35	3136.39
k_6	1.86	-2.98
SSE	4.0	4.6
$AARD$ (%)	15	18

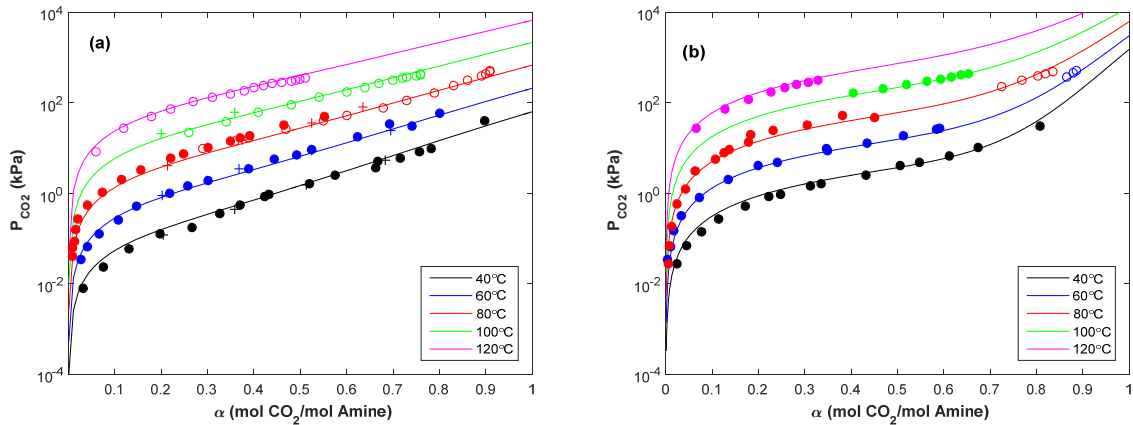


Figure 4. CO₂ solubility in aqueous solution at different loadings and temperatures a). 50 mass% 2-PPE b). 40 mass% 1-(2HE)PRLD (Open and closed circles, this work; +, (Chen and Rochelle, 2011); Solid lines, model prediction).

3.2. Physical properties measurements

The measured densities of unloaded and loaded solutions are presented in Tables 8 and 9, and viscosities are given in Tables 10 and 11.

As can be seen from the data, the densities and viscosities of both solutions increase with CO₂ loading and decrease with temperature, as expected. It should be noted that measurements at high loadings and high temperatures (above 65°C) were not possible in the setup used due to CO₂ desorption. Densities and viscosities for the 50 mass% 2-PPE measured in this work are in a good agreement with literature data (Paul and Mandal, 2006; Xu et al., 1992). No literature data were found for 40 mass% 12-HE-PRLD.

Table 8. Densities of 50 mass% 2-PPE solution at different loadings and temperatures

$\alpha \left(\frac{\text{mol CO}_2}{\text{mol Amine}} \right)$	<i>Density (kg/m³)</i>								
	20°C	25°C	30°C	40°C	45°C	50°C	60°C	70°C	80°C
0.00	1019.73	1016.33	1012.92	1009.50	1005.84	1002.28	998.58	991.03	983.19
	1019.74	1016.33	1012.91	1009.49	1005.83	1002.26	998.57	991.01	983.18
0.01	1037.91	1034.37	1030.87	1027.38	1023.56	1019.87	1015.92	1008.12	1000.24
	1037.92	1034.37	1030.86	1027.37	1023.54	1019.86	1015.91	1008.12	1000.22
0.15	1055.13	1051.52	1047.92	1044.25	1040.32	1036.47	1032.46	1024.56	1016.41
	1055.13	1051.52	1047.91	1044.24	1040.30	1036.45	1032.46	1024.55	1016.40
0.24	1071.33	1067.59	1063.79	1059.75	1055.50	1051.82	1047.87	1039.78	1031.57
	1071.33	1067.59	1063.78	1059.74	1055.49	1051.81	1047.87	1039.77	1031.56
0.31	1085.73	1081.75	1077.95	1074.05	1069.99	1065.89	1061.77	1053.58	1045.27
	1085.73	1081.75	1077.94	1074.03	1069.97	1065.88	1061.77	1053.56	1045.25
0.41	1102.16	1098.22	1094.17	1090.02	1085.88	1081.71	1077.45	1069.29	1060.95
	1102.16	1098.22	1094.16	1090.00	1085.86	1081.70	1077.45	1069.27	1060.93
0.46	1112.10	1108.10	1104.12	1099.98	1095.91	1091.63	1087.52	1079.34	1070.95
	1112.11	1108.10	1104.11	1099.96	1095.90	1091.62	1087.52	1079.33	1070.94
0.62	1131.87	1128.29	1124.62	1120.57	1116.99	1113.00	1109.19	1101.52	1093.55
	1131.88	1128.29	1124.61	1120.54	1116.97	1112.98	1109.19	1101.51	1093.53
0.81	1149.84	1146.96	1143.50	1140.13	1133.22	1131.04	1129.79	-	-
	1149.84	1146.96	1143.49	1140.12	1133.21	1130.69	1129.78	-	-

Table 9. Densities of 40 mass% 1-(2HE)PRLD solution at different loadings and temperatures

$\alpha \left(\frac{\text{mol CO}_2}{\text{mol Amine}} \right)$	<i>Density (kg/m³)</i>							
	20°C	25°C	35°C	45°C	55°C	65°C	75°C	80°C
0.00	1017.18	1013.83	1007.11	999.92	992.44	984.66	976.56	972.39
	1017.18	1013.84	1007.10	999.91	992.43	984.65	976.55	972.38
0.10	1035.17	1031.64	1024.49	1016.92	1009.08	1001.02	992.68	988.42
	1035.17	1031.65	1024.47	1016.90	1009.07	1000.99	992.67	988.41
0.30	1068.41	1064.75	1056.82	1048.29	1040.01	1031.67	1023.17	1018.86
	1068.42	1064.76	1056.81	1048.27	1039.99	1031.65	1023.15	1018.86
0.50	1098.51	1094.58	1086.53	1077.42	1069.05	1060.46	1052.42	1048.17
	1098.52	1094.59	1086.52	1077.41	1069.03	1060.46	1052.41	1048.17
0.70	1124.09	1120.19	1112.99	1103.87	1095.88	1088.02	-	-
	1124.09	1120.19	1112.98	1103.85	1095.86	1088.00	-	-

0.871	1140.69	1137.42	1130.75	1122.44	1115.10	-	-	-
	1140.70	1137.42	1130.74	1122.43	1115.08	-	-	-

Table 10. Viscosities of 50 mass% 2-PPE solution at different loadings and temperatures

$\alpha \left(\frac{\text{mol CO}_2}{\text{mol Amine}} \right)$	<i>Viscosity (mPa · s)</i>					
	20°C	30°C	40°C	50°C	60°C	70°C
0.00	17.07	10.34	6.74	4.69	3.38	2.57
	17.08	10.37	6.80	4.75	3.43	2.62
0.08	-	-	8.12	-	4.29	-
	-	-	8.19	-	4.36	-
0.16	21.00	-	-	-	-	-
	20.99	-	-	-	-	-
0.24	-	-	10.67	-	5.11	3.87
	-	-	10.82	-	5.20	3.91
0.41	29.30	-	13.79	-	6.50	4.84
	29.44	-	13.63	-	6.49	4.95
0.46	-	-	14.56	9.90	7.10	4.85
	-	-	14.72	10.22	7.87	5.05
0.62	39.45	-	16.66	-	7.87	6.13
	39.52	-	16.85	-	8.08	6.09
0.69	42.36	-	-	-	-	-
	42.45	-	-	-	-	-
0.81	47.89	-	-	-	-	-
	47.97	-	-	-	-	-

Table 11. Viscosities of 40 mass% 1-(2HE)PRLD solution at different loadings and temperatures

$\alpha \left(\frac{\text{mol CO}_2}{\text{mol Amine}} \right)$	<i>Viscosity (mPa · s)</i>					
	20°C	30°C	40°C	50°C	60°C	70°C
0.00	7.82	5.07	3.54	2.60	1.98	1.55
	7.83	5.09	3.56	2.62	1.99	1.57
0.10	8.20	5.35	3.75	2.78	2.01	1.60
	8.21	5.37	3.78	2.80	2.02	1.62
0.30	9.86	6.42	4.47	3.24	2.45	1.91
	9.87	6.44	4.50	3.28	2.48	1.93
0.50	12.37	8.03	5.57	3.88	2.89	2.27
	12.40	8.07	5.61	3.92	2.90	2.28
0.70	13.42	8.91	6.30	4.57	3.46	2.68
	13.43	8.95	6.35	4.61	3.49	2.72

The density of the loaded solutions is fitted to an empirical correlation reported in (Hartono et al., 2014):

$$\rho_{loaded}(\text{kg}/\text{m}^3) = \frac{\rho_{unloaded}}{1-w_{\text{CO}_2} \cdot (1-\theta)^n} \quad (12)$$

Where w_{CO_2} and θ are calculated as:

$$w_{CO_2}(\text{mass fraction}) = \frac{\alpha \cdot x_{Amine} \cdot MW_{CO_2}}{x_{Amine} \cdot MW_{Amine} + (1 - x_{Amine} - \alpha \cdot x_{Amine}) \cdot MW_{Water} + \alpha \cdot x_{Amine} \cdot MW_{CO_2}} \quad (13)$$

$$\theta(-) = \frac{b_1(-) \cdot \alpha \cdot x_{Amine} + b_2(-) \cdot x_{Amine}}{b_3 \left(\frac{\text{mol } CO_2}{\text{mol Total}} \right) + x_{Amine}} \quad (14)$$

Where b_1, \dots, b_3 are the parameters fitted for the density of loaded solutions; α, x_{Amine}, MW are the loading of solution, mole fraction of amine and molecular weight of amine, water or CO_2 , respectively.

Density of the unloaded amine solutions is fitted to the correlation:

$$\rho_{unloaded} \left(\frac{kg}{m^3} \right) = c_1 \left(\frac{kg}{m^3} \right) + c_2 \left(\frac{kg}{m^3 \cdot ^\circ C} \right) \cdot t(^{\circ}C) + c_3 \left(\frac{kg}{m^3 \cdot ^\circ C^2} \right) \cdot t(^{\circ}C)^2 \quad (15)$$

Where c_1, \dots, c_3 are the fitted parameters.

The parameters for the density correlations are given in Table 12. Figure 5 shows the experimental data and model representation for both solvents. The average absolute relative deviation is 0.05 and 0.06% for 2-PPE and 1-(2HE)PRLD, respectively, (Table 12) showing that the model is able to provide a good prediction of the density of both the loaded and unloaded solutions. It can be seen that density decreases with temperature but it increases with loading in a second order for both solvents.

Table 12. Parameters for the density correlations (eq. 12-15)

Parameter	2-PPE	1-(2HE)PRLD
w_{Amine}	50 mass%	40 mass%
x_{Amine}	0.1224	0.0945
b_1	4.31	4.48
b_2	-2.69	-2.10
b_3	0.85	1.42
c_1	1032.52	1029.50
c_2	-0.61	-0.59
c_3	-0.0013	-0.0016
MW_{Amine}	129.2	115.17
MW_{Water}	18.015	
MW_{CO_2}	44.01	
n	1	

<i>SSE</i>	0.00009	0.00005
<i>AARD (%)</i>	0.05	0.06

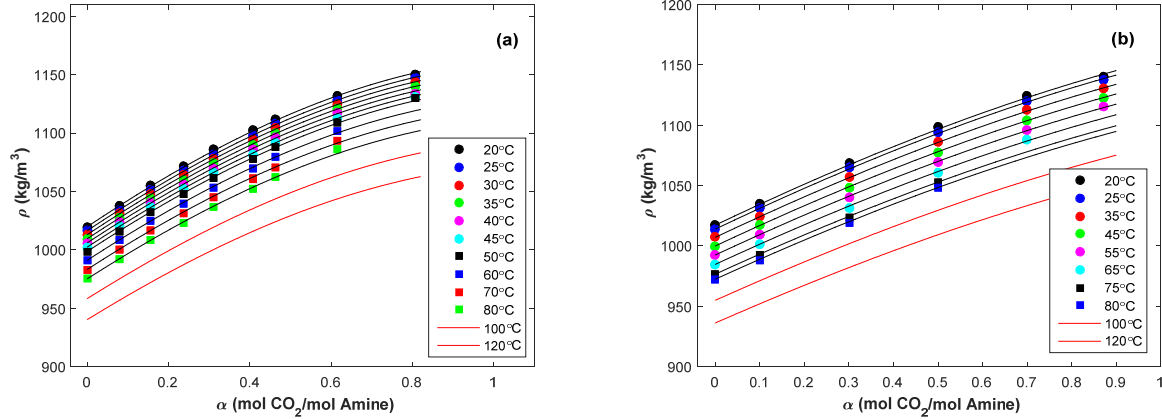


Figure 5. Densities of the 50 mass% 2-PPE (a) and 40 mass% 1-(2HE)PRLD (b) as function of temperature and CO₂ loading (Points, experimental data; Solid lines, model prediction).

The viscosities of 50 mass% 2-PPE and 40 mass% 1-(2HE)PRLD were fitted using correlations described by (Hartono et al., 2014):

$$\ln(\mu_{loaded})(mPa \cdot s) = (1 - x_3) \cdot \ln(\mu_{unloaded}) + x_3 \cdot \ln(\mu^*) \quad (16)$$

$$\ln(\mu^*)(mPa \cdot s) = \frac{f_1(-) \cdot \alpha \cdot x_{Amine} + f_2(-) \cdot x_{Amine}}{f_3\left(\frac{mol\ CO_2}{mol\ Total}\right) + x_{Amine}} \quad (17)$$

$$\ln(\mu_{unloaded})(mPa \cdot s) = \left[e_1(-) - \frac{e_2(K)}{e_3(K) + T(K)} \right] \quad (18)$$

Where e_1, \dots, e_3 and f_1, \dots, f_3 are the fitted parameters for viscosities of unloaded and loaded solutions; α, x_{Amine} are the loading of solution and mole fraction of amine, respectively.

The optimized parameters for the viscosity correlation for the both solvents are given in Table 13. The experimental data are compared with the model predictions in Figures 6 and 7. The 50 mass% 2-PPE solution is twice as viscous as the 40 mass% 1-(2HE)PRLD solution, while the 40mass% 1-(2HE)PRLD is found to be twice as viscous as the 30 mass% MEA (Hartono et al., 2014). Both models represent the experimental data for unloaded and loaded solutions up to 70°C

with good accuracy as seen from the Table 13 as well as in Figure 6 and Figure 7. A slightly increased deviation can be seen at 20°C and at high loadings for both solutions.

Table 13. Parameters for the viscosity correlations (eq. 16-18)

Parameter	2-PPE	1-(2HE)PRLD
w_{Amine}	50 mass%	40 mass%
x_{Amine}	0.1224	0.0945
Unloaded solution		
e_1	-3.39	-3.25
e_2	-703.74	-607.12
e_3	-180.72	-178.61
SSE	0.0004	0.0002
AARD (%)	0.5	0.3
Loaded Solution		
f_1	-1.73	0.52
f_2	5.62	5.49
f_3	-0.081	-0.038
SSE	0.1	0.09
AARD (%)	3.8	2.9

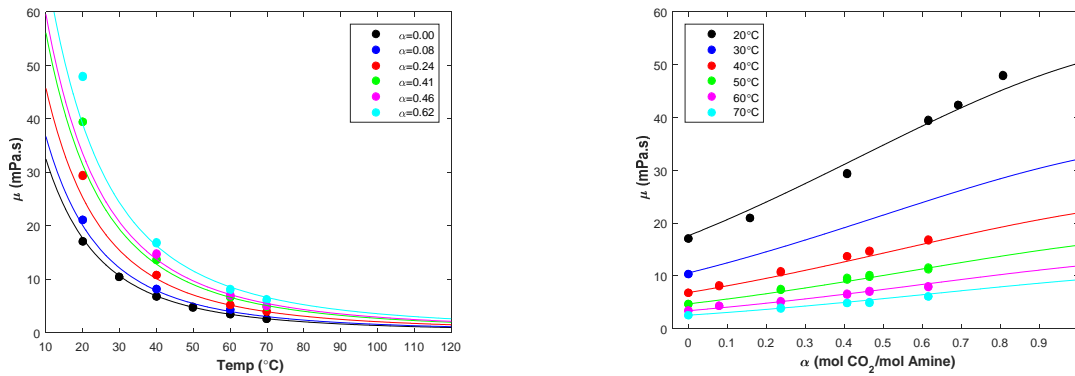


Figure 6. Viscosity in aqueous solution of 50 mass% 2-PPE at different temperatures and loadings (Points, experimental data; Solid lines, model prediction).

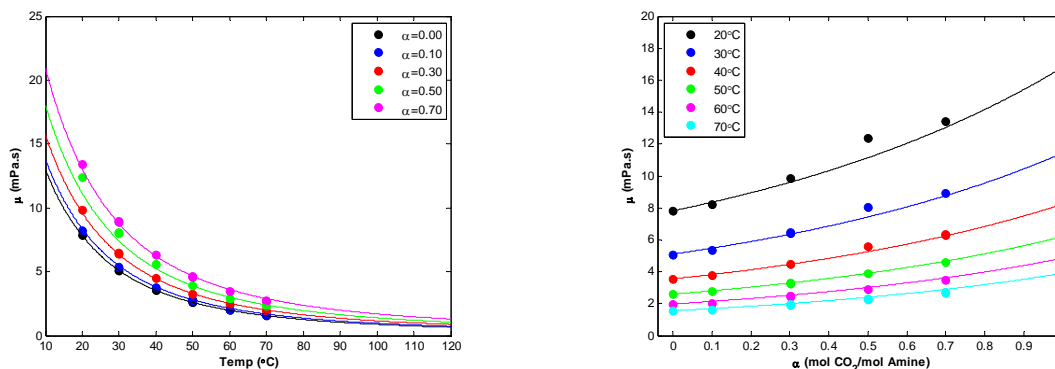


Figure 7. Viscosity in aqueous solution of 40 mass% 1-(2HE)PRLD at different temperatures and loadings (Points, experimental data; Solid lines, model prediction).

3.3. Solvent degradation measurements and environmental properties tests

The results from the oxidative degradation tests for 30 mass% 2-PPE and 30 mass% 1-(2HE)PRLD are compared with data for 30 mass% MEA (Vewelstad et al., 2014) in Figure 8. For the 30 mass% 1-(2HE)PRLD the result indicates that degradation took place; however, the loss was within the level of uncertainty. The 30 mass% MEA gives around 10% loss after 3 weeks, (Vewelstad et al., 2013), while almost 60% of the 2-PPE was degraded during the same period.

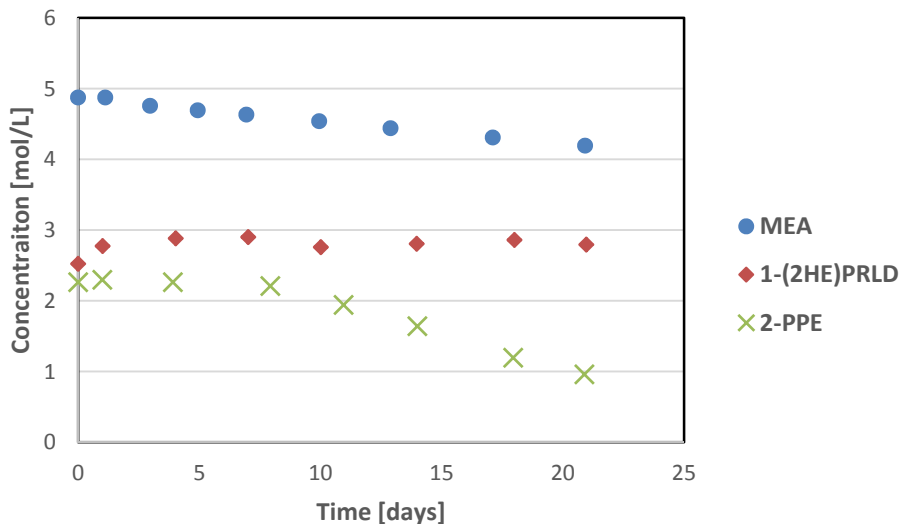


Figure 8. Loss of 2-PPE and 1-(2HE)PRLD in oxidative degradation (55 °C) compared to data for 30 mass% MEA (Vevelstad, 2013)

The concentrations of some of the degradation compounds (ammonia, pyrrolidine and N-nitrosopyrrolidine (NPyr), measured for some of the samples, are presented in Table 14. The degradation compounds are only observed in small amounts. Nitrosamine was quantified as NPyr for 1-(2HE)PRLD and as total Nitrosamine for 2-PPE. The highest amount of NPyr was observed in the initial sample, taken from the reactor around 30 minutes after start-up. The concentration however decreased from the initial to the end sample. Since only limited information is available in the literature on nitrosamines formation for other amines, no conclusion can be made about whether the nitrosamine formation would be a problem with the studied amines. Nevertheless, possible nitrosamine formation should be taken into account in future work. Only a small amount of ammonia was measured in the samples and in the gas leaving the reactor. For 1-(2HE)PRLD, the loss of amine due to ammonia formation is estimated to be less than 0.5%, while for 2-PPE, about 4% of the amine loss can be explained by ammonia formation.

Table 14. Concentration of degradation compounds measured in the oxidative degradation experiments (NA = Not Analyzed).

Amine	1-(2HE)PRLD, mmol/L			2-PPE, mmol/L	
	C _{NH3} [mmol/L]	C _{Pyrrolidine} [mmol/L]	C _{NPyr} [μmol/L]	C _{NH3} [mmol/L]	C _{total Nitrosamine} [μmol/L]
1	<0.6	0.1	0.0042	<0.6	NA
4	<0.6	NA	NA	2	NA
6	<0.6	NA	NA	9	NA
8	<0.6	0.5	0.00085	12	0.19

Results from the thermal degradation test for the two solvent systems tested in this work are compared to data for 30 mass% MEA in Figure 9.

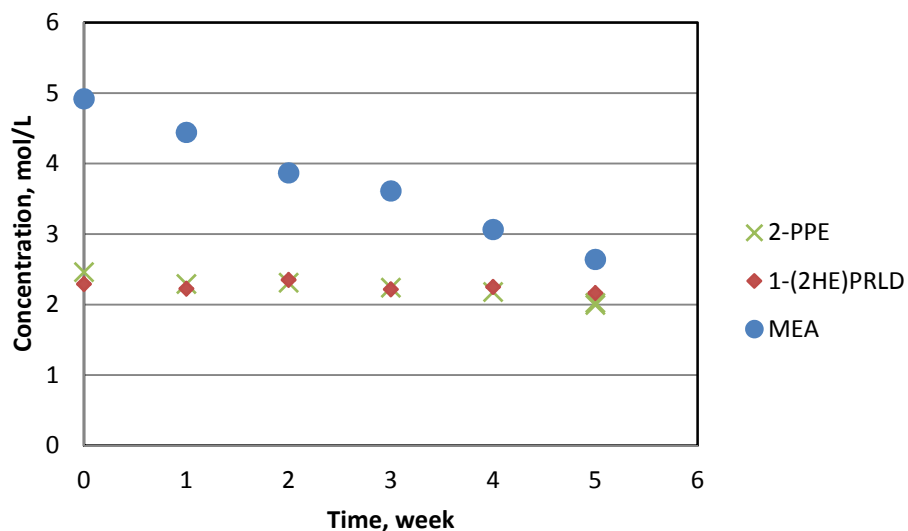


Figure 9. Loss of 30 mass% 2-PPE and 30 mass% 1-(2HE)PRLD in the thermal degradation test (135°C) compared to data from 30 mass% MEA (Vevelstad, 2013).

The overall degradation of amines studied in this work was below 6% for 1-(2HE)PRLD and 18% for PPE, which is low compared to 30 mass% MEA, that has shown more than 50% loss in 5 weeks at the same conditions (Eide-Haugmo, 2011). Tertiary amines are usually more stable with regard to carbamate polymerization than primary or secondary alkanolamines or polyamines. Since 1-(2HE)PRLD is a cyclic tertiary alkanolamine, it is expected to degrade less under these experimental conditions.

The results from the ecotoxicity tests for the two amines tested in this work are presented in Table 15. The amines showed EC_{50} values ranging from 14.8 (± 1.2) mg/l to 202.3 (± 1.1) mg/l with the two species. 1-(2HE)PRLD was slightly more toxic than 2-PPE, and the phytoplankton species was more sensitive than the copepod species to both chemicals. The results from the biodegradation tests in freshwater are compared to the value for reference amine (aniline) in Figure 10.

Table 15. EC- values (\pm standard error) of 1-(2HE)PRLD and 2-PPE . The results are shown as the concentrations that caused reduction on algal growth rates or copepod mobility by 10% (EC_{10}), 50% (EC_{50}) and 90% (EC_{90}). The EC_{50} -results are marked in bold.

Chemical	1-(2HE)PRLD			2-PPE		
	EC_{10} ; mg/L	EC_{50}; mg/L	EC_{90} ; mg/L	EC_{10} ; mg/L	EC_{50}; mg/L	EC_{90} ; mg/L
Phytoplankton (EC)	0.5 \pm 1.6	14.8\pm1.2	439.5 \pm 1.5	23.3 \pm 1.3	43.8\pm1.1	82.2 \pm 1.2
Copepods (LC)	107.2 \pm 1.1	143.2\pm1.1	191.9 \pm 1.2	162.6 \pm 1.1	202.3\pm1.1	251.8 \pm 1.1

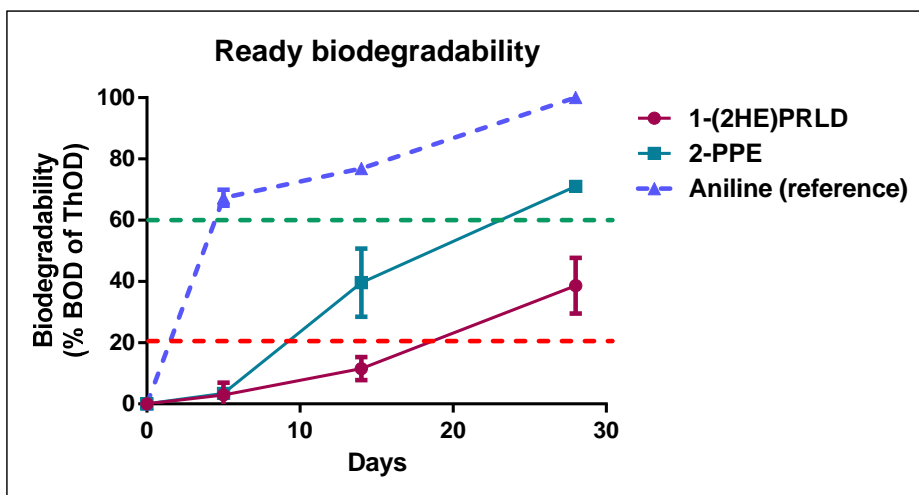


Figure 10. Biodegradability of 1-(2HE)PRLD, 2-PPE and the reference compound aniline in a freshwater BOD test at 20°C during a period of 28 days. The limits for ready biodegradability (60%; green line) and "non-degradability" (20%; red line) are shown. Error bars show standard error.

Environmental properties of the 2-PPE and 1-(2HE)PRLD are compared to the properties of the most widely used amines (MEA, 2-amino-2-methyl-1-propanol (AMP), and piperazine) in Table 16. It may be seen from the table that 1-(2HE)PRLD is slightly more toxic than 2-PPE, while both amines are more toxic than MEA or AMP and piperazine. It should be noted that no specific threshold levels for ecotoxicity exist for chemical emissions from carbon capture facilities. However, for discharges from the offshore industry (EC_{50}) a limit of 10 mg/L has been

established by the Oslo-Paris Commission (HOCNF, 2013). Neither 1-(2HE)PRLD nor 2-PPE was more toxic than 10 mg/L, and toxicities were thus below this threshold limit. Biodegradability test results showed that 2-PPE can be considered ready biodegradable (> 60% biodegradability), while 1-(2HE)PRLD and MEA are moderately biodegradable according to the method used in this work. For comparison, AMP and piperazine are considered not degradable due to very low biodegradability values measured at similar conditions (Eide-Haugmo, 2011).

Table 16. Environmental properties of the tested chemicals

Amine	Ecotoxicity (EC ₅₀ , mg/L)	Biodegradability (% BOD of ThOD, 28 days)	Color code*
1-(2HE)PRLD	14.8 ± 1.2	38.6	Yellow
2-PPE	43.8 ± 1.1	71.0	Yellow
MEA	198	68	Yellow
AMP	119	3	Red
Piperazine	472	1	Red

* Adopted from OSPAR convention (HELCOM-29/2008, 2008)

3.4. Potential of the studied solvents

2-PPE has been found to have a high absorption capacity (Figure 4 and (Hartono et al., 2017)) and acceptable environmental properties (Table 16). Furthermore, 2-PPE has been reported to have a moderate kinetic rate ((Sartori and Savage, 1983); (Hartono et al., 2017)) and is expected to have lower heat of absorption than MEA (Chowdhury et al., 2013b). However, 2-PPE is more viscous than that of MEA (Figure 6) and the oxidative degradation. Nitrosamine formation was observed after day 8 in the oxidative degradation experiments (Table 14 and Figure 8).

The 1-2(HE)PRLD as tertiary amine has also been shown to have a high cyclic capacity (Figure 4 and (Hartono et al., 2017)) and it was found to be chemically stable toward degradation (Figure 8 and 9), non-toxic and biodegradable (Table 16). The drawback could be attributed to a low reaction rate ((Liu et al., 2016; Liu et al., 2017)) therefore an activator would be required.

4. Conclusion

Aqueous solutions of two sterically hindered amines, 2-piperidineethanol (2-PPE) and 1-(2-hydroxyethyl)pyrrolidine (1-2(HE)PRLD), were tested in this work as promising solvents for CO₂ capture. The VLE data both solvents were measured at temperatures between 40 and 120 °C at different CO₂ loadings. Densities and viscosities of unloaded and CO₂-loaded solvents systems were measured between 20 and 80 °C. The VLE data and the physical properties data for both systems are fitted to simple correlations as functions of temperature and loading. The models predict the density and viscosity data with an AARD value less than 1 and 4% correspondingly, while for the VLE data the AARD is around 16%. The thermal degradation tests showed that both 1-(2HE)PRLD and 2-PPE are more stable and less corrosive than MEA. The oxidative degradation rate of 1-(2HE)PRLD is lower than that of 30mass% MEA, while 2-PPE shows much higher oxidative degradation compared to MEA. The ecotoxicity and biodegradability tests of the two amines 1-(2HE)PRLD and 2-PPE showed that both amines are not toxic ($EC_{50} < 10$ mg/l) and biodegradable (BOD > 20%).

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Appendix A

Details with regard to column, ion source and mobile phase for the experiment.

Table A1: Conditions for the different analyses.

	1-(2HE)PRLD, 2-PPE and Pyrrolidine	N-nitrosopyrrolidine	Ammonia
Ion source	ESI	APCI	ESI
Column/mobile phase	a	a	b
Dilution	1/10000	1/1000	
Internal standard	No	No	Yes
Derivatization	No	No	Yes

^aAscentis Express RP – Amide HPLC Column (15cm x 4.6 mm, 2.7 μ m, Cat#:53931-U, Supelco Analytical, Bellefonte, USA); Mobile phase: 25 mM formic acid + methanol in gradient.

^bAscentis Express C18 (15 cm x 2.1 mm, 2.7 μ m, Cat#:53825-U, Supelco Analytical, Bellefonte, USA); Mobile phase: 25 mM formic acid + acetonitrile in gradient

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