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Carbon Capture with 4 m Piperazine/4 m 2-Methylpiperazine

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Abstract

An equimolar diamine blend of 4 m 2-methylpiperazine (2MPZ) with 4 m piperazine (PZ) is shown to be an attractive solvent for CO_2 capture. This blend overcomes the difficulties posed by the narrow solid solubility window of pure 8 m PZ while preserving its benefits. The solid solubility window at 20 °C broadens from $P^*_{CO_2} = 0.10$ to $P^*_{CO_2} = 0.011$. As the blend viscosity is nearly double that of pure PZ, normalizing the capacity by viscosity shows a practical capacity comparable to MEA at 0.63 mol CO_2/kg solvent. The CO_2 absorption rate of the blend is lower, with $k'_{g,avg} = 7.1 \, x 10^7 \, mol/s \cdot Pa \cdot m^2$ at 40 °C, 84% that of PZ. The heats of CO_2 absorption of the blend and PZ are equal at $\Delta H_{abs} = -70 \, kJ/mol$. While the blend thermal stability is decreased, $T_{max} = 155$ compared to 163 °C, oxidative stability is similar. Lastly, their volatilities are nearly equal with amine Henry's constant near 23 Pa at 40 °C. In short, the equimolar blend of 4 m 2MPZ with 4 m PZ is a competitive solvent for amine scrubbing.

Keywords: amine scrubbing; diamine solvent; absorption; stripping; solvent characterization

1. Introduction

Concentrated (8 molal (m)) piperazine (PZ) is an attractive solvent for CO_2 capture by amine scrubbing because it absorbs CO_2 twice as fast as 7 m monoethanolamine (MEA), has 1.8 times the intrinsic capacity of 7 m MEA, is resistant to oxidation, and can be regenerated at 150 °C/8 bar without significant thermal degradation [1]. However, at 0 °C, 8 m PZ will precipitate PZ·6H₂O solid at less than 0.3 mol CO_2/equiv PZ and ⁺HPZCOO⁻ solid at greater than 0.42 mol CO_2/equiv PZ. The blend of 4 m PZ with 4 m 2-methylpiperazine (2MPZ) promises to minimize problems with solids precipitation while maintaining the other desirable properties of 8 m PZ [2].

Previous amine scrubbing work has focused on using aqueous, concentrated piperazine (PZ) and PZ blended with methyldiethanolamine (MDEA)/PZ [3, 4]. The fast kinetics of PZ made it a promoter in previous blends such as MDEA/PZ and monoethanolamine (MEA)/PZ, where its concentration was 0.5 to 2.5 m PZ. 2MPZ has two amine groups, one of which is hindered as shown in Figure 4 [5]. This paper reports measurements with 2MPZ and 4 m 2MPZ/4 m PZ of

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solid solubility, thermal and oxidative degradation, vapor-liquid equilibrium, volatility, hydraulic properties, and reaction kinetics. A review of PZ blends with other diamines is given by Li *et al* [6].

2. Materials and Methods

2.1. Solution Preparation

Aqueous solutions were made by adding anhydrous piperazine (Sigma-Aldridge, 98% pure) or 2MPZ (AK Scientific, 98% pure) to DDI water. The solution was then sparged with CO_2, and the heat of reaction and loading rendered the whole system liquid. Loading was measured gravimetrically [7].

2.2. Total Inorganic Carbon (TIC) for Loading

Samples were gravimetrically diluted up to 100× according to the predicted CO_2 concentration. 20−30 μL of the diluted sample was injected into 30 wt % H_3PO_4 to free the carbon dioxide. A stream of N_2 carried the CO_2 to an IR analyzer (Model 525, Horiba PIR 2000), whose voltage was monitored using Picolog software. At the end of each run, calibration was performed by injecting a known amount of carbon dioxide (1000 ppm carbon, Ricca Chemical Company, Arlington, TX). This calibration relates the voltage peak area to carbon mass fraction. The loading was determined with an estimated accuracy of 0.5−1% [7].

2.3. Titration for Amine Concentration

Samples were gravimetrically diluted ~300x prior to titration using an automatic Titrando titrator with equivalence point detection (Metrohm, Riverview, FL, USA) . Using 0.2 N H_2SO_4, samples were titrated to pH 2.4. The acid used to reach an equivalence point near a pH of 3.9 was used to determine total amine concentration [8].

2.4. Viscosity

The viscosity was measured using a Physica MCR 300 cone and plate rheometer (Anton Paar GmbH, Graz, Austria). The angular speed of the cone was varied to change the shear rate from 100 to 1,000 s^{-1} with each shear rate lasting 10 s. The shear stress was measured ten times, and the average value is reported [7].

2.5. Thermal Degradation

Solvent was loaded into and sealed in an ~10 mL stainless steel cylinder. At least six cylinders were used per run. The initial weight was recorded and used to guard against excessive mass loss. The samples were then analyzed using HPLC and cation and anion chromatography for quantification of degradation products and extent of degradation [9].

2.6. Oxidative Degradation

Oxidative degradation was studied using a semi-batch low-gas flow (LGF) reactor with batch liquid and continuous 2% CO_2 in oxygen gas [7-9]. The reactor temperature was 70 °C, and vigorous agitation was used to provide adequate mass transfer to the solution. Various metal ions added as their sulfate salts were used to mimic the effect of corrosion in an industrial system. In early experiments only iron (Fe) or iron, nickel, and chromium (SSM) was added. Later, manganese was added to the mix.

Liquid samples were taken over a two-week period and analyzed for formate and formamides (the sum of which is referred to as total formate). Total formate was determined by treating the samples with an equal volume of 5 N NaOH, waiting 24-48 hours, and analyzing for formate by anion chromatography [8].

2.7. Vapor-liquid Equilibrium

A batch reactor with gas recycle through a hot gas FTIR was used to measure VLE and amine volatility. Amine concentration between 0.3 and 4 m is measured. In order to create a calibration curve, 2MPZ and PZ had to be diluted with DI water and the spectra of water was subtracting from the resulting curve to yield a calibration curve. CO_2 was sparged into the bottom of a temperature-controlled, glass reactor with a mixer. The headspace is continuously sampled using a 180 °C sample line, then the gas returns to the headspace [10]. The reported experimental error in vapor phase measurements is ±2% [11].

2.8. Wetted-Wall Column (WWC)

Vapor-liquid equilibrium and mass transfer rate data were collected by counter-currently contacting a water-saturated N_2/CO_2 gas stream with an aqueous amine solution. Both absorption and desorption were measured by varying the CO_2 inlet partial pressure [5]. The overall mass transfer coefficient can be found from:

$$\text{Flux} = K_G \left(P_{CO_2,\text{bulk}} - P^*_{CO_2} \right) \tag{1}$$

$$\frac{1}{K_G} = \frac{1}{k_g} + \frac{1}{k'_g} \tag{2}$$

Then, using K_G with prior measurement and correlation of k_g, the liquid-side resistance can be found [12]. k'_g can be used to rank the rate of CO_2 absorption of amines.

3. Results

3.1. Solid Solubility

Solid solubility of PZ has been studied for a range of loading, temperature, and concentration, while 4 m 2MPZ/4 m PZ has been studied for a range of temperature and loading. Solutions were allowed to equilibrate by stirring before slowly adjusting the temperature. The temperature was ramped at 1 °C every 5 minutes, and the transition temperature was marked when the last precipitate melted. Aqueous 2MPZ is liquid at room and elevated temperatures for all loading, so blending it with PZ widens the solid solubility window, as shown in Figure 1 and tabulated in Table 1. The solubility is represented as a function of the equilibrium CO_2 partial pressure at 40 °C, a surrogate for CO_2 loading. The rich solubility limit is temperature-insensitive, whereas the lean limit is highly sensitive. At 0 °C the 4 m 2MPZ/4 m PZ has an operating window from 0.3 to 20 kPa CO_2, making it acceptable for CO_2 capture from most sources, including coal-fired power plants.
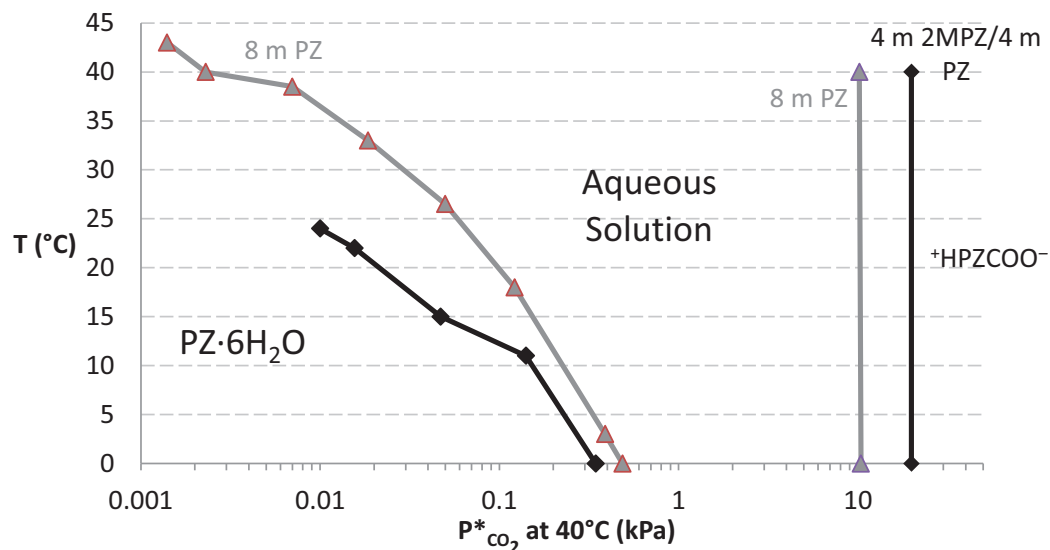
Figure 1 Solid solubility of 8 m PZ and 4 m 2MPZ/4 m PZ [13].

Table 1 Transition Temperatures for 8 m PZ and 4 m 2MPZ/ 4 m PZ [13].

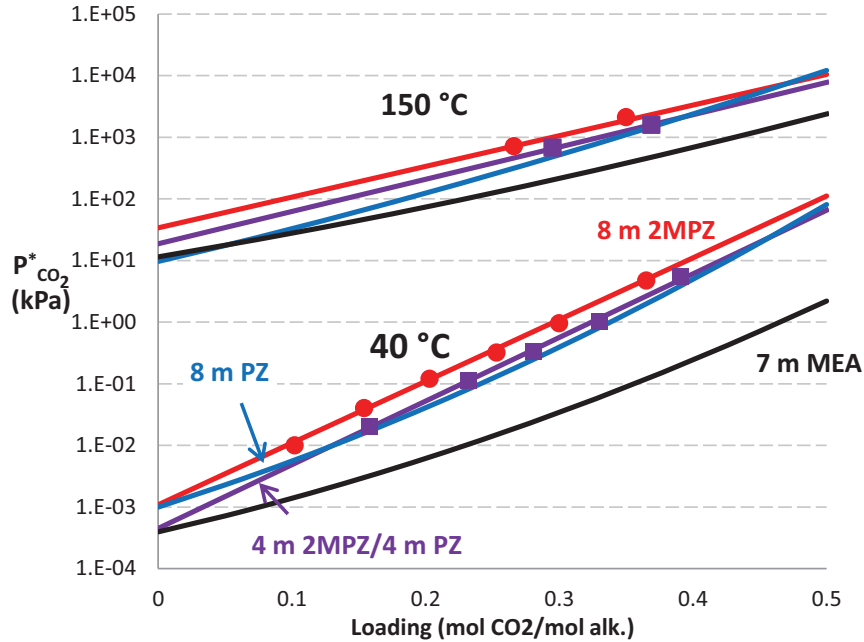| Amine (m)	CO$_2$ Loading $\left(\frac{mol\ CO_2}{mol\ alk.}\right)$	$P^*_{CO_2}$ at 40 °C (kPa)	Transition T (°C)
	0.000	0.0014	43.0
	0.035	0.0023	40
	0.104	0.007	38.5
	0.158	0.0185	33
	0.209	0.050	26.5
8 PZ	0.251	0.1220	18
	0.303	0.39	3
	0.313	0.49	0
	0.454	10.2	40
	0.441	10.4	0
	0.088	0.100	23
	0.108	0.0156	21.5
4 2MPZ/4 PZ	0.159	0.047	17.5
	0.209	0.141	11
	0.250	0.345	0
	0.450	19.9	40
	0.450	19.9	0

3.2. CO₂ Solubility

Figure 2 CO₂ solubility. The points are experimental data (40 °C [12], 150 °C [14]), and the curves are predictions from Equation (3).

The solubility of CO_2 in 4 m 2MPZ/4 m PZ is shown in Figure 2. The data are fit with the semi-empirical Equation (3), where P is in Pa and α is loading in $mol\ CO_2/mol\ alk.$ Heat of absorption is calculated using the Gibbs-Helmholtz equation, Equation (4). Table 6 shows that while 2MPZ has greater capacity than PZ, the diamine blend capacity lies almost exactly between them.

$$\ln P_{CO_2} = a + \frac{b}{T} + d\alpha^2 + e\frac{\alpha}{T} + f\frac{\alpha^2}{T} \qquad (3)$$

$$\Delta H_{abs} = -R\frac{d\left(ln\ P^*_{CO_2}\right)}{d\left(1/T\right)} \qquad (4)$$

Table 2 Parameter values for Equation (3) [14].

	MEA	PZ	2MPZ	2MPZ/PZ
a	38.6±0.4	35.3±0.3	39.9±0.8	40.1±0.8
b	-12379±139	-11054±120	-9923±50	-12807±266
d	-16.0±2.5	-18.9±2.7	0	0
e	3556±231	4958±347	13990±905	14114±837
f	8702±932	10163±1085	0	0
R^2	0.994	0.993	0.999	0.999

Table 3 CO_2 solubility in 4 m 2MPZ/4 m PZ. For the total pressure data, the blend is equimolar but total molality is 7.63 m for *, and the rest are 7.86 m [14]. The remaining data is from [12].

T (°C)	CO_2 loading ($mol/mol\ alk.$)	$P_{CO_2}^*$ (kPa)	P_{Total} (kPa)
40	0.15	0.02	
	0.232	0.11	
	0.281	0.33	
	0.33	1.01	
	0.391	5.44	
	0.158	0.17	
	0.232	0.64	
60	0.281	2.01	
	0.33	5.39	
	0.391	22.83	
80	0.158	1.03	
	0.232	3.63	
	0.281	8.58	
	0.33	23.95	
100	0.158	4.19	
	0.232	15.75	
	0.397	227	315
120	0.306	142	316*
	0.389	576	750
130	0.303	252	489*
	0.384	837	1073
140	0.3	427	744*
	0.376	1201	1517
150	0.295	673	1091*
	0.369	1585	2001
160	0.288	1011	1554*
	0.359	2084	2624

3.3. Viscosity

The viscosity of 2MPZ was measured from 0.0 to 0.4 mol CO_2/mol alk. at 40, 50, and 60 °C. The viscosity of 4 m 2MPZ/4 m PZ was measured from 0.04 to 0.3 mol CO_2/mol alk. for the same temperatures. In Figure 3, all viscosity is shown at 40 °C and a nominal rich loading. 2MPZ is nearly twice as viscous as equal concentration PZ, and blending has negligible effect.

As an increase in the molality of the solvent is commensurate with an increase in both capacity and viscosity at different rates, and as too high a solvent viscosity reduces mass and heat transfer rates, a novel metric called the viscosity-normalized capacity is proposed as defined in Equation (5). This metric balances the drawback of increased viscosity against increased capacity with increasing molality to achieve a more realistic capacity. The blend has a viscosity-normalized capacity of is 0.63 compared to 0.77 mol CO_2/kg solvent of 8 m PZ, showing that the increased viscosity is makes the solvent capacity on par with 7 m MEA.

$$Capacity_{\mu-norm} = Capacity * \left(\frac{\mu}{10 \text{ Cp}} \right)^{-0.25} \tag{5}$$
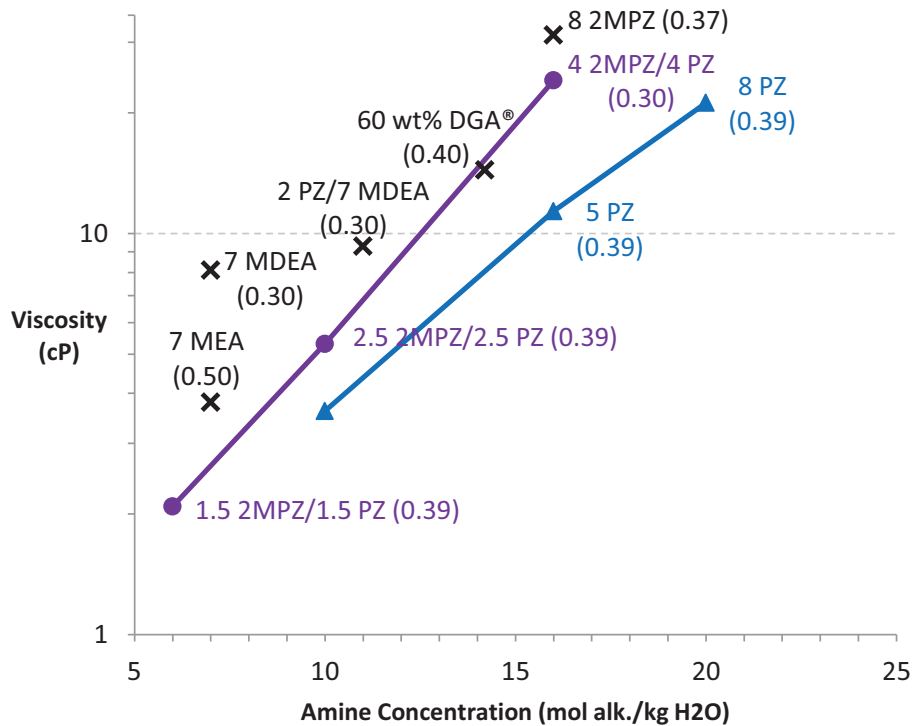

Figure 3 Comparison of amine viscosity at 40 °C and nominal rich loading. The labels read like so: "7 MEA (0.50)" means 7 molal MEA at its rich loading of 0.50 [3, 12].

3.4. Thermal Stability

Thermal degradation was measured with 0.30 mol CO_2/mol alk. at 150 °C for a period of thirty weeks with 8 m 2MPZ, 8 m PZ, and 4 m 2MPZ/4 m PZ. As observed with other methylated or di-methylated PZ derivatives, 2MPZ is more susceptible to thermal degradation while 2MPZ/PZ lies between the two pure amines, as shown in Figure 4. Table 6 shows the maximum regeneration temperature resulting in a loss of 2% of the initial solvent per week.

3.5. Oxidative Stability

Total formate concentration in oxidation in the low gas flow reactor for 8 m PZ, 4 m 2MPZ/4 m PZ, and 7 m MEA are shown in Figure 5. These results indicate that pure PZ and the blend are far more stable to oxidative degradation than 7 m MEA.
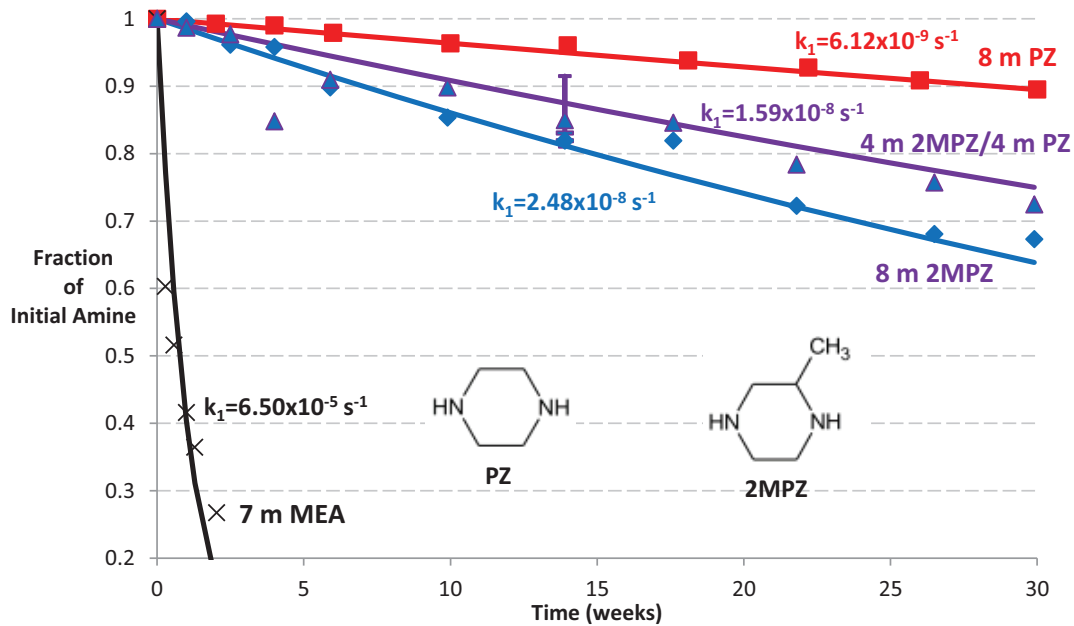
Figure 4 Thermal degradation of amines at 150 °C with 0.30 mol CO_2/mol alkalinity except for MEA which is 0.40 [15, 7]. The points are data, while the lines are exponential fits of the form $\frac{F_{am}}{F_{am,o}} = \exp(k_1 \times t)$ [7].
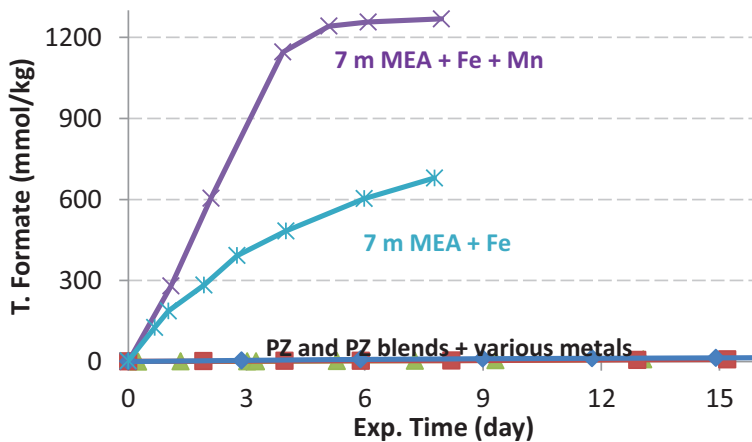

Figure 5 Production of total formate in amines in the LGF reactor at 70 °C vortexed with 2% CO_2 in oxygen.

Table 4 Total formate rate calculated from the final sample only. LGF reactor at 70 °C vortexed with 2% CO_2 in oxygen.

Solvent	T. Formate rate (mmol/kg/hr)	Amine loss rate (mmol/kg/hr)
7 m MEA + Fe + Mn	6.65	16.1
7 m MEA + Fe	3.64	11.9
8 m PZ + SSM	0.031	<0.3
8 m PZ + SSM + Mn	0.026	<0.3
4 m 2MPZ/ 4 m PZ + SSM + Mn	0.019	<0.3

3.6. CO_2 Absorption Rate

The rate of CO_2 absorption was studied using a wetted wall column. This rate is quantified as k'_g, which is the liquid-side mass transfer coefficient based on the partial pressure driving force. Data for 40 and 60 °C for 2MPZ, PZ, and the blend are shown in Figure 6 and tabulated in Table 5. The $k'_{g,avg}$ of 4 m 2MPZ/4 m PZ is 84% of 8 m PZ; the $k'_{g,avg}$ of 8 m 2MPZ is 70% of 8 m PZ, as shown in Table 6.
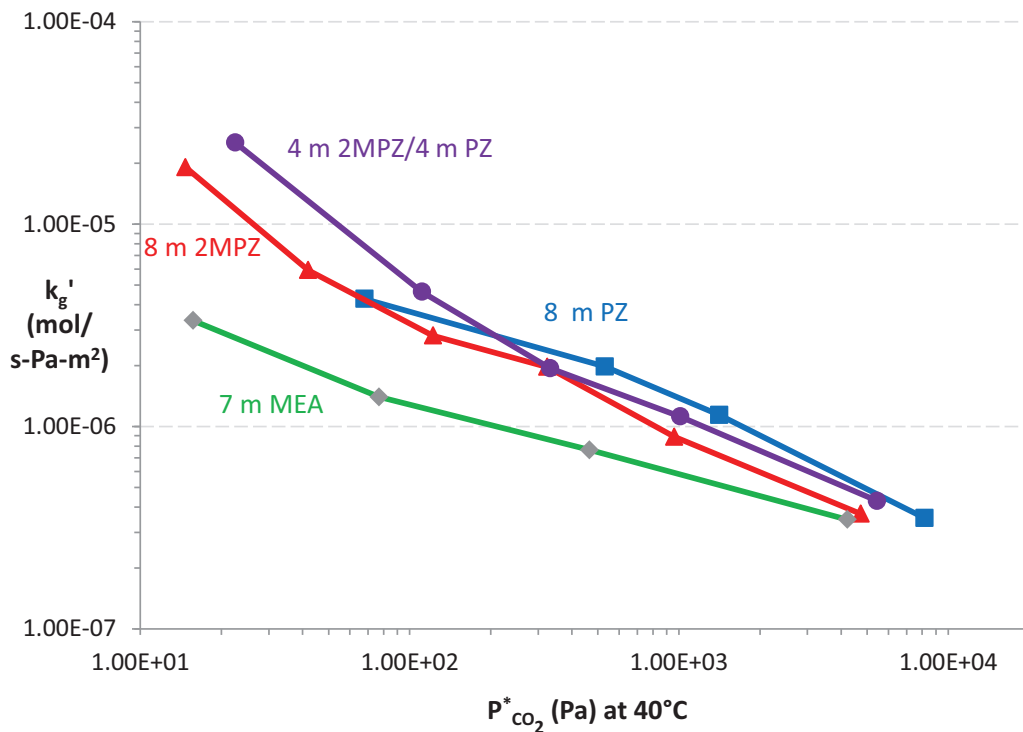

Figure 6 Rate of absorption for PZ, 2MPZ, 2MPZ/PZ at 40 °C [12].

Table 5 WWC data. 7 m MEA data are from [16], the remainder from [12].

Amine (m)	T (°C)	$P^*_{CO_2}$ (Pa)	k'_g (mol/s-Pa-m^2)	Amine (m)	T (C)	$P^*_{CO_2}$ (Pa)	k'_g (mol/s-Pa-m^2)
8 PZ	40	68	4.27E-06		40	22.5	2.53E-05
	40	530	1.98E-06		40	111	4.63E-06
	40	1409	1.14E-06		40	332	1.94E-06
	40	8153	3.53E-07		40	1010	1.12E-06
	60	430	4.41E-06		40	5440	4.29E-07
	60	2407	2.20E-06		60	169	6.28E-06
	60	7454	9.57E-07		60	635	4.01E-06
	60	30783	3.20E-07	4 2MPZ/ 4 PZ	60	2012	1.85E-06
8 2MPZ	40	14.7	1.91E-05		60	5388	1.40E-06
	40	42	5.92E-06		60	22831	2.83E-07
	40	122	2.81E-06		80	1026	6.16E-06
	40	324	1.97E-06		80	3632	2.82E-06
	60	961	8.89E-07		80	8583	1.61E-06
	60	4732	3.70E-07		80	23950	7.37E-07
	60	85	9.17E-06		100	4189	4.46E-06
	60	290	5.02E-06		100	15746	1.94E-06
	80	861	2.25E-06		40	15.7	3.34E-06
	80	2255	1.68E-06		40	77	1.40E-06
	80	4874	9.76E-07		40	465	7.66E-07
	80	22414	2.77E-07		40	4216	3.47E-07
	80	592	6.28E-06		60	109	2.92E-06
	80	1801	4.14E-06	7 MEA	60	660	1.70E-06
	80	4063	2.41E-06		60	3434	9.28E-07
	80	9715	1.37E-06		60	16157	3.76E-07
	80	22060	7.38E-07		80	1053	2.85E-06
	100	2679	5.12E-06		80	4443	1.87E-06
	100	7394	2.90E-06		100	5297	2.98E-06
	100	18648	1.49E-06		100	19008	1.40E-06

3.7. Volatility

While PZ and 2MPZ have lower normal boiling points (146 °C, 155 °C) than MEA (170 °C), all three amines have approximately the same volatility in aqueous systems. This is due to the non-ideality of PZ and 2MPZ in water [10]. Figure 7 shows the amine apparent Henry's constant normalized by amine concentration. In 4 m 2MPZ/4 m PZ diamine, the amines are less volatile than in their separate aqueous systems. This could be due to favorable interactions between the two amines, leading to reduced activity coefficients. Overall, the volatilites of the blend and 8 m PZ are nearly equal with H_{am}=23 Pa at 40 °C.
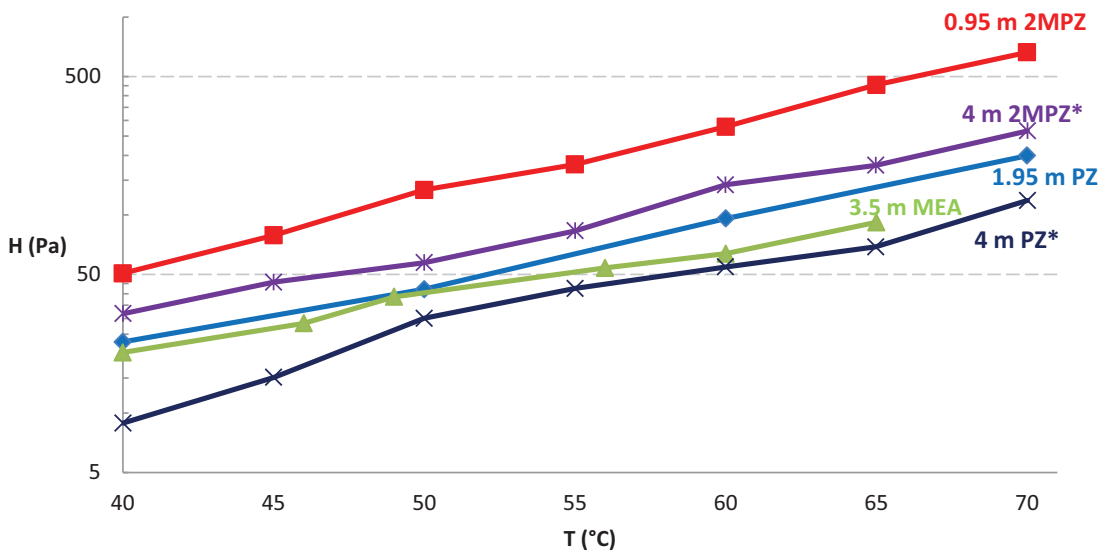
Figure 7 Unloaded amine volatilities in aqueous systems normalized by amine concentration [17]. $H_{am} = {P_{am}}/{x_{am}}$. Note that 2MPZ* and PZ* are the Henry's constants of the amines when blended.

4. Conclusion

Equimolar 4 m 2MPZ/4 m PZ is an attractive solvent for CO_2 capture because it widens the solid solubility window at 20°C from $P_{CO_2}^* = 0.10$ to $P_{CO_2}^* = 0.011$ while preserving many of the benefits of concentrated, aqueous PZ, as shown in Table 6. It has a viscosity-normalized capacity of 0.63 compared to 0.77 mol CO_2/kg solvent for 8 m PZ, while k_g' is 84% that of pure PZ. The heat of absorption in the blend and PZ are equal ($\Delta H_{abs} = -70 \; kJ/mol$), and while the blend thermal stability is decreased (T_{max} = 155 compared to 163 °C), oxidative stability is similar. The blend volatility is nearly the same as 8 m PZ (H_{am}=23 Pa at 40 °C). Taken together, the equimolar blend of 4 m 2MPZ with 4 m PZ is a competitive solvent for amine scrubbing. Using the data assembled here, a thermodynamic and kinetic model can be constructed to compare equivalent work and economics of this blend against other solvents.

Table 6 Amine properties. Capacity is calculated from the change in equilibrium CO_2 partial pressure from 5 kPa to 0.5 kPa at 40 °C [12]. The loading range values correspond to these extremes. $-\Delta H_{abs}$ is calculated from Equation (4). The μ-norm capacity is calculated by Equation (5). T_{max} is approximately the stripper temperature leading to a loss of 2% of the initial solvent per week [7]. $k_{g,avg}'$ is defined as the log mean flux of CO_2 divided by the log mean driving force, or $k_{g,avg}' = N_{CO_2,LM}/\left(P_{CO_2,gas} - P_{CO_2}^*\right)_{LM}$.

Amine (m)	Capacity $\left(\dfrac{mol \; CO_2}{kg \; solvent}\right)$	Capacity$_{\mu\text{-norm}}$ $\left(\dfrac{mol \; CO_2}{kg \; solvent}\right)$	Loading range $\left(\dfrac{mol \; CO_2}{mol \; alk.}\right)$	$-\Delta H_{abs}$ at $P_{CO_2}^* = 1.5$ kPa $\left(\dfrac{kJ}{mol}\right)$	T_{max} (°C)	$k_{g,avg}'$ at 40°C $\left(\dfrac{x10^7 mol}{s - Pa - m^2}\right)$
7 MEA	0.47	0.60	0.45−0.55	82	122	4.3
8 PZ	0.79	0.77	0.31−0.39	70	163	8.5
8 2MPZ	0.93	0.70	0.27−0.37	72	151	5.9
4 2MPZ/4 PZ	0.84	0.63	0.30−0.39	70	155	7.1

Acknowledgements

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