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CO₂ absorption into aqueous amine blended solutions containing monoethanolamine (MEA), N,N-dimethylethanolamine (DMEA), N,N-diethylethanolamine (DEEA) and 2-amino-2-methyl-1-propanol (AMP) for post-combustion capture processes

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HIGHLIGHTS

- CO₂ absorption into aqueous amine blended solutions containing MEA, AMP, N,N-DMEA, and N,N-DEEA.
- Overall CO₂ mass transfer co-efficients in blends similar to those in standalone MEA solutions.
- CO₂ absorption and cyclic capacities predicted using chemical equilibrium modelling tool.
- Significant increase in cyclic capacity in amine blends compared to MEA at similar concentrations.

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ABSTRACT

Presently monoethanolamine (MEA) remains the industrial standard solvent for CO₂ capture processes. Operating issues relating to corrosion and degradation of MEA at high temperatures and concentrations, and in the presence of oxygen, in a traditional PCC process, have introduced the requisite for higher quality and costly stainless steels in the construction of capture equipment and the use of oxygen scavengers and corrosion inhibitors. While capture processes employing MEA have improved significantly in recent times there is a continued attraction towards alternative solvents systems which offer even more improvements. This movement includes aqueous amine blends which are gaining momentum as new generation solvents for CO₂ capture processes. Given the exhaustive array of amines available to date endless opportunities exist to tune and tailor a solvent to deliver specific performance and physical properties in line with a desired capture process. The current work is focussed on the rationalisation of CO₂ absorption behaviour in a series of aqueous amine blends incorporating monoethanolamine, N,N-dimethylethanolamine (DMEA), N,N-diethylethanolamine (DEEA) and 2-amino-2-methyl-1-propanol (AMP) as solvent components. Mass transfer/kinetic measurements have been performed using a wetted wall column (WWC) contactor at 40 °C for a series of blends in which the blend properties including amine concentration, blend ratio, and CO₂ loadings from 0.0–0.4 (moles CO₂/total moles amine) were systematically varied and assessed. Equilibrium CO₂ solubility in each of the blends has been estimated using a software tool developed in Matlab for the prediction of vapour liquid equilibrium using a combination of the known chemical equilibrium reactions and constants for the individual amine components which have been combined into a blend.

From the CO₂ mass transfer data the largest absorption rates were observed in blends containing 3 M MEA/3 M Am₂ while the selection of the Am₂ component had only a marginal impact on mass transfer rates. Overall, CO₂ mass transfer in the fastest blends containing 3 M MEA/3 M Am₂ was found to be only slightly lower than a 5 M MEA solution at similar temperatures and CO₂ loadings. In terms of equilibrium behaviour a slight decrease in the absorption capacity (moles CO₂/mole amine) with increasing Am₂ concentration in the blends with MEA was observed while cyclic capacity followed the opposite trend. Significant increases in cyclic capacity (26–111%) were observed in all blends when compared to MEA

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solutions at similar temperatures and total amine concentrations. In view of the reasonable compromise between CO₂ absorption rate and capacity a blend containing 3 M MEA and 3 M AMP as blend components would represent a reasonable alternative in replacement of 5 M MEA as a standalone solvent.

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1. Introduction

1.1. Background

Increasing awareness surrounding the onset of climate change over the past decade due to rising CO₂ emissions in the atmosphere is driving a concerted effort to decrease our dependencies on the generation of electricity from the combustion of fossil fuels. It is clear a transition from fossil fuel fired power generation towards renewable energy/zero emission technologies is required in the future, however the clear absence of large scale, reliable, and robust technologies demands a clean-up of current coal fired power stations in the meantime in order to fulfil current ongoing electricity requirements (Abu-Zahra et al., 2007; Feron, 2010). Reductions in CO₂ emissions can be realised in the short term through the deployment of post-combustion capture (PCC) which (in its most common form) operates by contacting flue gas exiting the power station containing CO₂ with an amine solvent, before its emission into the atmosphere. Once separated, the remaining gas (mainly N₂) is released to the atmosphere while the relatively pure captured gas (CO₂ purity ~99%) is compressed and designated for sequestration. Recent studies have shown that underground storage of the separated gas in depleted oil and gas fields as well as in un-minable coal seams, are feasible options (White et al., 2003). The application of PCC to the coal fired power generation sector is additionally made attractive due to the flexibility to adapt the technology to existing power stations as well as a direct incorporation into the design of future installations, thus increasing up-take of the technology. However, despite the potential of such applications current PCC processes are viewed as economically unattractive and must be improved to ensure they are competitively placed as a cost effective option for CO₂ emissions reductions (Wang et al., 2011). One possible method to address these issues is to improve the efficiency of the chemical solvent employed in the capture process. The current industrial standard solvent MEA has remained the benchmark since its inception for acid–gas purification processes some 100 years ago, mainly due to its rapid reaction kinetics with CO₂ and simplicity of operation (Rochelle, 2009). However, several challenges with the use of MEA exist including:

- Degradation of the solvent in the presence of O₂, SO_x, and NO_x species (Chi and Rochelle, 2002; Supap et al., 2006).
- Concentration limited to ~30% w/w in the absence of corrosion inhibitors (Goff and Rochelle, 2004, 2006; Veawab and Tontiwachwuthikul, 2001).

Direct replacement of the solvent is a significant challenge given that MEA is among the fastest reacting amines (few solvents compete with MEA and offer realistic advantages in terms of reaction kinetics) while several other alternatives which offer favourable thermodynamic capacities for CO₂, for example the tertiary amine methyl-diethanolamine (MDEA) and sterically hindered amine 2-amino-2-methyl-1-propanol (AMP), are kinetically slower (Ume et al., 2012). An alternative approach is to implement MEA into a blended solvent with additional amine components (Mandal et al., 2001). The use of amine blends is conceptually simple and such mixed amine solvents have been suggested previously where a fast reacting amine, Am₁ (for example MEA), is combined in a blend with a tertiary/sterically hindered amine, Am₂, which is typically a stronger base and acts to

accept protons (H⁺) released from the reaction of CO₂ with amine and water (Xiao et al., 2000). Eq. (1) illustrates the reaction pathway of a fast reacting amine, Am₁, that forms carbamate. Eq. (2) illustrates the slower reaction pathway of a tertiary or sterically hindered amine, Am₂. Eq. (3) represents the situation of an amine blend in which Am₂ is a stronger base than Am₁.

The conceivable advantage of this situation is larger concentrations of the fast reacting amine for the direct reaction with CO₂ while the second amine performs the proton accepting role. The use of such a blended solvent has several advantages over single amine systems:

- Improved thermodynamic efficiency (higher equilibrium capacity of tertiary/sterically hindered amines promoting HCO₃⁻ formation combined with rate promoting amine) (Sakwattanapong et al., 2005).
- Reduction in issues relating to degradation and operation of the solvent caused by corrosion.
- Flexibility in the range of amines available to tailor and optimise the composition of the solvent to achieve the highest absorption efficiency.
- High absorption rates observed in single amine solvents can often be maintained in blends of the individual components.
- Energy requirement for solvent regeneration can be reduced (Bougie and Iliuta, 2012; Yih and Shen, 1988).

Despite the substantial number of investigations focussing on blended amine solvents for CO₂ capture processes, (Idem et al., 2006) the bulk of which have typically targeted promotion of CO₂ absorption in solutions containing <30% w/w sterically hindered and tertiary amines, (Mandal and Bandyopadhyay, 2006) few studies have focussed on the use of blends at high total amine concentrations above the typical 30% w/w concentration. Substantial improvements in the thermodynamic efficiency of a blended solvent can be achieved by increasing the concentration of amine in solution (Freeman et al., 2010). In this way larger absorption capacities can be achieved and/or lower solvent volumes can be used for a similar amount of CO₂ transport (loading) as that observed in lower concentration solvents. However, a trade-off in CO₂ absorption rates can often exist in concentrated amine systems relating to decreased diffusion of CO₂ due to increases in viscosity. The situation is particularly pertinent at high CO₂ loadings where viscosity tends to be largest. In an effort to understand the intimate CO₂ absorption behaviour in amine blends at higher total amine concentrations we have investigated the underlying effects of blend composition on the physical properties including density and viscosity, absorption rates, and CO₂ solubility in concentrated amine blends containing MEA and tertiary/sterically hindered amines as blend components.

1.2. Outline

CO₂ absorption and mass transfer into concentrated aqueous blends incorporating monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), N,N-dimethylethanolamine (DMEA), and N,N-diethylethanolamine (DEEA) as blend components, has been explored. The selection of these amines is justified based on their simple chemical structures and ideal chemical properties (basicities are suitable for use with MEA). The effect of MEA and tertiary/sterically hindered amine concentration, amine component ratios, and CO₂ loading on CO₂ mass transfer in each of the amine solutions has been investigated experimentally using a wetted wall column (WWC) contactor at 40 °C. Vapour liquid equilibrium predictions using a software tool developed in Matlab (Puxty and Maeder, 2013) have been used to determine CO₂ solubility in the amine blends at typical temperatures representing those which could otherwise be observed in a traditional capture process.

1.3. Theory

1.3.1. Chemical reaction set

The absorption of CO₂ in aqueous solutions can be described by the following reaction sets which incorporate the series of CO₂ hydration reactions and those describing the formation of amine-carbamates. Initially, and before reaction, CO₂ must dissolve across the gas-liquid interface. The equilibrium concentration of dissolved CO₂ is related to the Henry's constant for CO₂ solubility in water, and the partial pressure of the gas above the solution as described in the following equation:

$$H_{\text{CO}_2} = \frac{p_{\text{CO}_2}}{c_{\text{CO}_2}} = 2.82 \times 10^6 e^{-2044/T} \quad (4)$$

where H_{CO_2} represents the Henry's constant for CO₂ solubility in water at infinite dilution (kPa M⁻¹), p is the partial pressure of CO₂ in the gas phase above the solution, and c_{CO_2} is the dissolved concentration of CO₂ in the liquid (aqueous) phase, respectively (Crovetto, 1991).

Once dissolved, a series of parallel reactions ensue between CO₂(aq) and water (H₂O), hydroxide (OH⁻), and amine (R₁R₂NH where R₁ and R₂ are carbon/hydrogen atoms and/or larger side groups in the case of typical primary and secondary amines) to form carbonic acid (H₂CO₃), carbonate (CO₃²⁻), bicarbonate (HCO₃⁻), and/or carbamic acid/carbamate (R₁R₂NCO₂H/R₁R₂NCO₂⁻) respectively (Conway et al., 2011). The kinetic reactions are described in the following equations:

The chemical composition of the amine solutions are strongly influenced by the solution pH and CO₂ loading (moles CO₂ absorbed/mole amine) (Conway et al., 2012). Thus, the kinetic reactions must be coupled to the additional series of instantaneous protonation equilibrium including that of hydroxide (OH⁻), carbonate (CO₃²⁻), bicarbonate (HCO₃⁻), carbamate (RNHCO₂⁻), and amine (RNH₂) as described in Eqs. (8)–(12). From an equilibrium point of view the formation of carbamate (carbamate stability constant) can be described by an equilibrium reaction between bicarbonate and amine as shown in Eq. (13). The kinetics of this reaction have also been observed by ¹H NMR spectroscopy under specific conditions, (Conway et al., 2011; McCann et al., 2009)

however the significantly slower rate of this reaction in competition with reactions (6) and (7) was found to have a negligible impact on the analysis of absorption flux data obtained from absorption measurements in a wetted wall contactor and kinetic stopped-flow measurements (Puxty and Rowland, 2011). Thus this reaction appears exclusively in the equilibrium chemical model together with the following reactions.

In the case of blended amine solutions containing two amines the overall chemical model is assembled from the equilibrium reactions for each of the individual amines. For example the overall reaction set in a blend containing MEA and DMEA incorporates Eqs. (4)–(12) describing the diffusion of CO₂ and series of hydration reactions, formation of carbamate and protonation of the amine, and an additional term to describe the interaction of protons (H⁺) with the tertiary amine DMEA (Eq. 11).

1.3.2. Ionic strength

Activity co-efficient corrections were applied in the calculation of equilibrium concentrations using Specific Ion Interaction Theory (SIT) which incorporates a Debye-Hückel like term for activities and additional interaction parameters to describe short range interactions between ion pairs. It was previously found that in concentrated amine solutions setting the interaction parameters c_j and ϵ_{ij} to zero gave good agreement between VLE measurements and chemical models (Puxty and Maeder, 2013), and as such this was also done in this work. Thus, all data corresponds to standard state conditions at infinite dilution (i.e. zero ionic strength). The SIT expression used in this work is shown in Eq. (14) where γ_i is the activity co-efficient, $A = (1.8248 \times 10^6)/(eT)^{3/2}$ is the Debye-Hückel law slope, ρ is the density of water (kg dm⁻³), I is the ionic strength (mol dm⁻³), and z_i is the charge of species i

$$\lg_{10}\gamma_i = \frac{z_i^2 A \sqrt{I}}{1 + 1.5 \rho^{-1/2} \sqrt{I}} + \sum_{j=i}^{ns} c_j \in i_j \quad (14)$$

1.3.3. Mass transfer theory

CO₂ absorption flux into each of the blends at various CO₂ loadings was investigated over a range of CO₂ partial pressures. A representative series of absorption flux data as a function of the gas phase CO₂ partial pressure (Pa) into a solution containing 3.0 M MEA and 3.0 M DEEA over a range of CO₂ loadings from 0.0 to 0.4 (mole CO₂/mole amine) is shown in Fig. 1. Complete lists of CO₂ absorption flux and driving force data can be found in Table S2 in the supplementary materials section.

In solutions where absorption was measured to be less than 0.50% CO₂ the point was omitted due to limits in the accuracy of the instrumentation. This was the particular case at low CO₂ partial pressures. Overall linear correlations of the flux data were found to have an R -squared error value for all fits of at least $R^2 > 0.980$, and typically $R^2 > 0.99$. The overall mass transfer coefficient (K_G) can be extracted from the slope of the absorption flux as a function of CO₂

Fig. 1. Absorption flux, N_{CO_2} , as a function of applied driving force at 40.0 °C in blend containing 3.0 M MEA and 3.0 M DEEA and CO_2 loadings from 0.0–0.4 mol CO_2 /mole amine. Solid lines are linear trends through the data.

Fig. 2. Schematic of wetted-wall column contactor setup (Wei et al., 2014).

partial pressure (driving force) as in Fig. 1 and according to the following equation:

$$K_G = \frac{N_{\text{CO}_2}}{P_{\text{CO}_2,g} - P_{\text{CO}_2}^*} \quad (15)$$

where N_{CO_2} is the CO_2 flux, $P_{\text{CO}_2,g}$ is the CO_2 partial pressure in the gas phase and $P_{\text{CO}_2}^*$ is the equilibrium CO_2 partial pressure of the loaded amine which is constant at a given CO_2 loading. Since the value of $P_{\text{CO}_2,g}$ varies over the height of the column due to absorption, the value of the CO_2 driving force over the entire column is typically calculated as the logarithmic mean of the inlet and outlet CO_2 partial pressures respectively and as is the case here.

The overall mass transfer coefficient is a function of both the gas side (k_g) and liquid side (k'_g) mass transfer coefficients as

defined by the following equation:

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{1}{k'_g} \quad (16)$$

In this work the contribution of gas side mass transfer to K_g was neglected as independent measurements of SO_2 absorption by 30 wt% MEA has found that $k_g \gg k'_g$, even for fast reacting amines with gas flow rates of 1 L min^{-1} . Thus $K_g \approx k'_g$ for the gas flow conditions used.

2. Experimental methods

2.1. Chemicals

Monoethanolamine (MEA, Sigma-Aldrich, 99%), N,N-dimethylethanolamine (N,N-DMEA, Sigma-Aldrich, 99%), N,N-diethylethanolamine (N,N-DEEA, Sigma-Aldrich, 99%), 2-amino-2-methyl-1-propanol (AMP, Sigma-Aldrich, > 95%) were purchased from Sigma-Aldrich and used without purification. The structures of the amines selected for this study, and the protonation constants of the amines at 25.0 °C, are shown in Table 1. Carbon dioxide (CO_2 , 99.99%) and nitrogen gases (N_2 , 99.99%) were purchased from coregas Australia. All amine solutions were prepared using de-ionised water and volumetric glassware.

2.2. Wetted-wall column (WWC)

A general schematic of the wetted-wall column contactor is shown in Fig. 2. Briefly, the apparatus is comprised of a stainless steel column with an effective height and diameter of 8.21 and 1.27 cm respectively. Amine solution contained in a liquid reservoir submerged in a temperature controlled water bath (initially charged with ~0.5 L of amine solution) is pumped up the inside of the column before exiting through small outlet holes in the top of the column. Liquid exiting the top of the column flows over the sides and downwards in a thin film under gravity before collecting at the base and returning to the reservoir in a closed loop. Thus, the liquid flowing over the column is continuously replenished with solution from the reservoir which acts to minimise any changes in the composition of the solution from CO_2 absorption during the measurements. The temperature of the column and surrounding gas space was maintained by a jacketed glass sleeve connected to the water bath. All experiments were performed at atmospheric pressure.

The total liquid flow rate within the apparatus was maintained at $121.4 \text{ mL min}^{-1}$ (2.02 mL s^{-1}) as indicated by a calibrated liquid flow meter (Cole Parmer PMR1-010442). A mixed CO_2/N_2 gas was prepared by adjustment of Bronkhorst mass flow controllers for CO_2 and N_2 respectively. The mass flow controllers were routinely calibrated using a Drycal portable flow calibration unit (MesaLabs). Total gas flow rate in the system was maintained at 3.00 L min^{-1} . Prior to entering the column the gas stream was passed through a 1/8" steel coil and saturator located in a water bath. Liquid and gas flow rates were chosen so as to maintain a consistent and free flowing liquid film during operation.

The amount of CO_2 absorbing into the amine liquid was determined from the CO_2 content of the gas stream entering (bottom) and exiting (top) the column. The former was measured while bypassing the absorption column with the gas stream passing directly to the gas analyser. Absorption flux, N_{CO_2} , was determined in each of the amine solutions (including CO_2 loaded solutions) over a range of CO_2 partial pressures typically spanning 1.0–20.0 kPa. The concentration of CO_2 in the gas stream entering and exiting the column was monitored via a Horiba VA-3000 IR gas analyser. The gas analyser was calibrated routinely using a

Table 1
Amines.

Chemical name	Abbreviation	Structure	Protonation constant (25 °C)
Monoethanolamine	MEA		9.44
N,N-dimethylethanolamine	N,N-DMEA	monoethanolamine (MEA)	9.23
N,N-diethylethanolamine	N,N-DEEA	N,N-Dimethylethanolamine (NN-DMEA)	9.80
2-Amino-2-methyl-1-propanol	AMP	N,N-Diethylethanolamine (NN-DEEA)	9.67
		2-amino-2-methyl-1-propanol (AMP)

Fig. 3. Physical property data for a blend containing 3 M MEA, 3 M DMEA (left) viscosity (right) density.

series of standard calibration gases spanning 1–25% (BOC gases Australia). CO₂ loaded amine solutions were prepared by bubbling a pure CO₂ gas stream into a known volume of amine solution with the resulting mass change of the solution as measured using a Mettler Toledo PB4002-S balance (± 0.01 g) to determine the final CO₂ loading. To ensure loss of amine or water did not affect the measured mass a condenser was attached to the outlet flask and any condensate returned directly to the flask below ensuring the mass change was equivalent only to the amount of CO₂ delivered to the amine solution.

2.3. Density and viscosity

Densities and viscosities of the amine solutions were determined using a combined Anton Paar DMA-38 density meter (± 0.001 g/ml) and AMVn viscometer (± 0.001 mPa/s). Density and viscosity measurements were performed in triplicate with the final value reported here as the average of these repeats.

2.4. Vapour liquid equilibrium (VLE) estimations

Equilibrium CO₂ solubility in each of the blends has been estimated here using an equilibrium modelling tool developed in Matlab (Puxty and Maeder, 2013).

The tool functions by predicting the overall chemical speciation in the amine blends using the equilibrium reactions which describe the interactions of CO₂ with all reactive species in solution. Following calculation of the equilibrium speciation, the partial pressure of CO₂ in the gas above the solution can be calculated from the predicted concentration of dissolved (free) CO_{2(aq)} in solution and the Henry's constant for CO₂ solubility in water.

CO₂ absorption capacity at 40 °C, expressed in units of moles of CO₂/total moles of amine, at constant CO₂ partial pressure (15 kPa), was calculated for each of the blends. Similarly, cyclic capacities were calculated from the absolute difference in CO₂ loading at 40 and 100 °C at constant CO₂ partial pressure (15 kPa). We are aware the above conditions do not necessarily represent the true energy optimum in a realistic capture process, however they nevertheless allow for a general and consistent comparison of the equilibrium behaviour for the purposes of screening in the blends here.

3. Results and discussion

3.1. Density and viscosities of amine blends

The overall assessment of a solvent for CO₂ capture requires knowledge of physical properties of the amine solution, the values

of which are often integrated into calculations of diffusion parameters in process models and in the practical design of heat exchangers and absorption contactors. Measured densities and viscosities of the amine blends over the temperature range 25–40 °C and CO₂ loadings from 0.0 to 0.4 mol CO₂/mole amine for blends containing 3 M MEA and 3.0 M Am₂, and 25–40 °C and CO₂ loadings from 0.0 to 0.3 mol CO₂/mole amine for the remaining blends, are available in Table S1 of the supplementary materials section. Selected density and viscosity data for a blend containing 3 M MEA 3 M DMEA is shown in Fig. 3. Generally, the density in the solutions were found to decrease linearly with temperature and increase exponentially with CO₂ loading while viscosity was found to both decrease and increase exponentially with respect to temperature and CO₂ loading. Density and viscosity in the blends was found to follow the order DMEA~AMP>DEEA and is largely independent of the MEA concentration. The trend in density and viscosity was found to increase with an increasing concentration of the Am₂ component in the blend. Overall, viscosities of the blends here were found to be larger than those observed in the standalone MEA solutions at similar temperatures, total amine concentrations, and CO₂ loadings. Additional molecular interactions in the blends stemming from the increase in molecular weight and sizes of the Am₂ components and interactions arising from ionic strength effects, particularly at higher CO₂ loadings, can account for the observed increases in viscosity. The physical properties of the blends here remain within a suitable range for PCC processes.

3.2. CO₂ absorption measurements

3.2.1. Absorption flux, N_{CO₂}

CO₂ absorption into a series of blended MEA solutions containing N,N-DMEA, N,N-DEEA, and AMP was investigated in this work using a wetted wall column contactor at 40 °C. The underlying impact of CO₂ loading on absorption was investigated by measuring absorption flux into the blended amine solutions after pre-loading the solutions with amounts of CO₂. In doing so, a range of conditions representing absorption at different regions along the length/height of the absorber, and absorption into CO₂ loaded solutions representing those returning from the desorber, can be expected. To permit a fair assessment of the effect of the blend components, absorption measurements into MEA solutions at identical total amine concentrations as present in the blends were performed in parallel.

3.2.2. Overall CO₂ mass transfer co-efficient(s)

Overall CO₂ mass transfer coefficients, K_G , were determined from plots of absorption flux, N_{CO₂}, against the applied driving force (P_{CO₂}, determined as the log mean of the inlet and outlet CO₂ partial pressures) in each of the blends where the linear slope is equal to the overall mass transfer co-efficient. The resulting overall mass transfer coefficients for each of the amine blends at 40 °C are presented in Table 2. Generally, CO₂ mass transfer was found to be dependent of MEA concentration, blend ratios, and CO₂ loading. In the case of the latter K_G was found to decrease consistently with increasing CO₂ loading in each of the blends. Such decreases are in line with depletion of the bulk concentration of free “reactive” amine upon loading (with CO₂) and increases in solution viscosity due to increasing amounts of charged species (carbonate, bicarbonate, protonated amine, carbamate, etc.) and the subsequent interactions of these species in solution. A thorough evaluation of the effects of blend ratio and Am₂ component selection on CO₂ mass transfer continues in the following sections.

Table 2

Overall CO₂ mass transfer co-efficients (K_G , mmol m⁻² s⁻¹ Pa) at 40.0 °C and CO₂ loadings from 0.0 to 0.4 mol CO₂/total mole amine. Note – data at 0.4 CO₂ loading only available for selected blends.

K_G (mmol m ⁻² s ⁻¹ kPa ⁻¹)	CO ₂ loading			
	0.0	0.1	0.3	0.4
Solution				
2 M MEA 2 M DMEA	1.91	1.75	0.85	–
2 M MEA 3 M DMEA	1.90	1.60	0.80	–
2 M MEA 4 M DMEA	1.86	1.56	0.77	–
3 M MEA 3 M DMEA	2.15	1.82	0.86	0.43
3 M MEA 3 M DEEA	1.93	1.56	1.00	0.45
2 M MEA 3 M DEEA	1.59	1.43	0.88	–
2 M MEA 4 M DEEA	1.45	1.31	0.56	–
3 M MEA 3 M AMP	2.06	1.76	0.96	0.38
2 M MEA 3 M AMP	1.92	1.38	0.74	–
2 M MEA 4 M AMP	1.86	1.47	0.63	–
4 M MEA	2.29	2.05	1.31	0.85
5 M MEA	2.57	2.15	1.41	0.88
6 M MEA	2.59	2.28	1.43	0.89

Fig. 4. Overall CO₂ mass transfer co-efficients, K_G , as a function of CO₂ loading at 40 °C in blends containing MEA and DMEA as blend components.

3.2.2.1. Effect of blend ratio on K_G . From the data in Table 2 highest CO₂ mass transfer rates were obtained in blends containing 3 M MEA with 3 M Am₂ components over the entire range of CO₂ loadings. It should be emphasised a blend containing 2 M MEA 2 M Am₂ will not offer any practical kinetic benefit over a 5 M MEA solution given the low MEA and overall amine concentrations respectively in such a blend. However, the data forms part of the series here and are of general interest to rationalise the rates of absorption with blend ratio. Selected data covering a range of blend ratios in solutions containing MEA and DMEA over a range of CO₂ loadings is shown in Fig. 4. Similar overall trends in K_G as a function of blend ratio and CO₂ loading are observed in the blends involving DMEA and AMP as Am₂ components.

The observed rates can be rationalised in terms of the individual contributions and behaviour of the blend components to CO₂ mass transfer. Firstly, overall K_G values for each of the blends containing 2 M MEA with varying amounts of Am₂ are similar over the CO₂ loading range. Given MEA is the only amine contributing directly to mass transfer (via fast and direct reaction with CO₂) it is not surprising to observe that an increase in the concentration of MEA from 2 M to 3 M, while maintaining the Am₂ concentration (representing only a 20% increase in total amine concentration), results in significant increase in K_G . The fastest rates were observed in blends containing 3 M MEA and 3 M Am₂ in each of the series. The data indicates that CO₂ mass transfer is relatively independent of the Am₂ concentration. For example, for the blends containing 2 M MEA increasing the Am₂ concentration from 2 to 3 to 4 M has little

Fig. 5. Overall CO_2 mass transfer co-efficient K_G as a function of CO_2 loading at 40°C in blends containing 3 M MEA and 3 M Am_2 .

Fig. 6. Overall CO_2 mass transfer co-efficients K_G for amine blends and corresponding MEA solutions at similar total amine concentrations (blue=4 M, blue=5 M, red=6 M). Note – data presented at 0.1 CO_2 loading. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

impact on the K_G values. While correct, it belies the fact that the physical and chemical properties of Am_2 have counteracting effects on CO_2 mass transfer that ultimately result in no net change. Increasing the concentration of Am_2 increases the viscosity of the blend, lowering the diffusion coefficients of both CO_2 and the amines and negatively impacting mass transfer. However, because Am_2 is a stronger base than MEA increasing its concentration increases its capacity to absorb protons from the CO_2 to MEA reaction, resulting in more free MEA remaining available to react. Additional Am_2 will also raise the pH of the blend increasing the OH^- concentration, but this effect is negligible as the OH^- concentration is several orders of magnitude lower than MEA.

3.2.2.2. Effect of Am_2 blend components on K_G . Selected CO_2 mass transfer data for blends containing 3 M MEA and 3 M Am_2 are presented in Fig. 5. From the figure K_G is seemingly independent of the Am_2 component in the blend and is essentially identical over the range of CO_2 loadings in each of the blends. This is not surprising given that MEA is the only active amine component in the blend contributing directly to mass transfer via direct reaction with CO_2 , and the similar chemical properties (protonation constants) of the Am_2 components. Furthermore, given the protonation of the amine is considered instantaneous (certainly on the timescale of the absorption process) for each of the Am_2 amines examined here the only distinguishing effect on CO_2 mass transfer from Am_2 in the blends stems from the diffusion of CO_2 into the solution and of Am_2 and MEA from the bulk solution to the interface to perform the proton accepting role, however this is likely to be negligible in the

wetted-wall due to the short liquid residence time. To this effect slightly higher rates (some 5%) were observed in blends containing DMEA and AMP over blends containing DEEA given the larger molecular weight and highly branched molecular structure compared to that of DMEA and AMP which ultimately results in larger viscosity and slower diffusion rates. Interestingly, despite DEEA being a stronger base than DMEA and AMP (thus it could be assumed the proton accepting role is correspondingly larger and higher concentrations of free MEA are made available for reaction) it appears this property has little observable impact on CO_2 mass transfer rates here and indicates the process is largely dominated by the role of MEA in its reaction with CO_2 . Mass transfer is similar in each of the amine blends above CO_2 loadings exceeding 0.2 mol CO_2 /total mole amine.

3.2.2.3. Overall comparison of K_G in blends with standalone MEA solutions at similar total amine concentrations. An important comparison involves the absorption performances of the blends with the corresponding MEA solutions at similar total amine concentrations. K_G values for standalone MEA solutions at corresponding conditions and total amine concentrations present in the blends have been determined in this work. K_G values for each of the amine blends together with the corresponding MEA solutions at 0.1 CO_2 loading is presented graphically in Fig. 6. From the figure K_G is lower in all blends when compared to the corresponding MEA solutions at similar concentrations. The smallest relative deviation in K_G was observed in a solution containing 2 M MEA and 2 M DMEA while the largest decrease was observed in a solution containing 2 M MEA and 4 M DEEA. The above can again be justified in terms of the physical properties of the solutions where low concentrations of Am_2 , and overall amine concentration in the former solution, results in lower viscosities and thus higher CO_2 diffusion and CO_2 mass transfer and vice versa for the latter. The average decrease in K_G over the 10 blends investigated is $\sim 27\%$ and indicates that a slight increase in the absorber sizing would be required to offset the slower reaction rates. Blends containing 3 M MEA and 3 M DMEA and AMP respectively result in the highest mass transfer rates and are only 15% lower than those observed in a 6 M MEA solution. Given the concentration of MEA is limited to ~ 5 M in the absence of corrosion inhibitors, the concentrated 6 M blends here represent effective alternative options to standalone MEA solutions without any significant penalty to mass transfer rates. Slight increases in absorption temperature will afford reaction rates and thus improved absorption performance.

3.3. Vapour liquid equilibrium (VLE) predictions

While the overall CO_2 absorption rate is an important property in the selection of a capture solvent it is one of only several properties which are critical in the specification of a capture process. In terms of the energy demand for desorption, consideration must be given to the thermodynamic efficiency and equilibrium CO_2 capacity of a solvent which are strongly correlated to the reboiler duty on the regeneration (desorber) side of the process. Further, lower solvent volumes and similar capture efficiencies, and thus lower energy demands per unit of CO_2 captured and desorbed over the entire process can be achieved in higher efficiency solvents. Estimations of the equilibrium CO_2 solubility in each of the amine blends have thus been performed here using independently determined chemical equilibrium data for the individual amines taken from our previous studies, which have been combined into a blend (Fernandes et al., 2012a, 2012b). The interested reader is directed to Figs. S1 and S2, of the supplementary materials sections for an example calculation of the equilibrium species concentration profile at 40°C , and calculated VLE curve at 40 and 100°C , as a function of CO_2 loading (expressed as

Fig. 7. Cyclic capacity in amine blends and MEA solutions; colours indicate total amine concentration; blue=4 M solution, green=5 M, red=6 M. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

moles CO₂/total mole amine) in a blend containing 3 M MEA and 3 M AMP respectively. A summary of the calculated absorption capacities at 40 °C and cyclic capacities (absolute difference in CO₂ loading at 15 kpa CO₂ partial pressure between 40 and 100 °C) for each of the blends are listed in Table S3 of the supplementary materials section and presented in Fig. 7.

As can be seen the absorption capacities of the blends and corresponding standalone MEA solutions are reasonably similar and independent of the Am₂ component and its concentration in the blend (when compared to the corresponding MEA solution at similar total amine concentration). This observation is not surprising and is consistent with the formation of the MEA–carbamate and it acting as a major CO₂ sink in both the blends and standalone MEA solutions. However, all of the amine blends demonstrated markedly higher cyclic capacities far in excess of the corresponding standalone MEA solvents (between 26% and 111% higher). The largest cyclic capacity was observed in a blend containing 2 M MEA/3 M AMP. The significantly better cyclic capacities can be rationalised in terms of the differences in the amine performing the proton accepting role (Am₂ in the case of the blend and MEA in the standalone solvent), in particular the enthalpy associated with the reversal of the protonation equilibrium of the amine. This point is emphasised in the blends containing AMP as the Am₂ component which has a larger enthalpy associated with the protonation equilibrium (more negative) and thus larger swings in this value with temperature. This behaviour ultimately results in larger overall swings in the solution pH and an increase in the cyclic capacity. It should be reiterated the conditions here do not necessarily represent the energy optimum and the ideal composition may change when the calculations are performed under the optimum operating conditions. Thus, detailed evaluations of the energy requirements are required to determine the optimum blend composition. This work is ongoing.

3.4. Additional considerations – degradation and corrosion behaviour

As stated throughout an extensive and multi-dimensional approach is required to exhaustively assess a capture solvent. The ideal solvent will not only address cost issues relating to investment and ongoing energy requirements through rapid kinetics and large CO₂ absorption and cyclic capacities, and materials compatibility, but will additionally address environmental and operational issues relating to oxidative and thermal degradation, corrosion, materials compatibility, toxicity, and precipitation to name a few. As an example it is anticipated that amine blends containing low MEA concentrations here, would go somewhat towards reducing the high corrosion rates observed in highly concentrated standalone

MEA solutions, however this requires further evaluation and validation beyond the scope of the work here.

4. Conclusions

CO₂ absorption behaviour in aqueous solutions containing MEA and 2-amino-2-methyl-1-propanol, N,N-dimethylethanolamine, and N,N-diethylethanolamine as blends components has been investigated and compared to absorption behaviour in standalone MEA solutions at similar concentrations. CO₂ Mass transfer rates in the blended solvents were slightly lower than those observed in standalone MEA solutions at similar total amine concentrations and CO₂ loadings. Absorption capacities in the blends were similar and comparable to standalone MEA solutions however the cyclic capacity of all of the blends was significantly higher than MEA solutions at similar total amine concentrations. In view of the reasonable trade-off between mass transfer and cyclic capacity we consider a blend containing 3 M MEA and 3 M AMP as the optimum solvent of those investigated here. While the fundamental measurement data and solvent properties addressed in this work can be used to guide the selection of solvents for use in practical capture applications, further assessment of the solvent properties is required to determine their overall suitability.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.ces.2014.12.053>.

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