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Promoting CO₂ absorption in aqueous amines with benzylamine

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Abstract

Post-combustion capture of CO₂ is the most mature technique for reducing greenhouse gas emissions from coal fired power stations. In this study, aqueous benzylamine (BA) was investigated as a potential solvent for CO₂ capture. First, CO₂ loading capacities in 30% wt/wt aqueous benzylamine were determined by vapour liquid equilibrium (VLE) experiment in a stirred vessel between 40 °C and 80 °C, over a pressure range up to 900 kPa. At 15 kPa and 40 °C, 0.45 mol CO₂/mol BA was absorbed. Protonation and carbamate thermodynamic equilibrium constants as well as the standard enthalpy of protonation were determined. Benzylamine showed a similar pK_a (8.89 at 40 °C) but a larger pK_a variation with temperature than MEA. The carbamate stability constant changed little with temperature. Benzylamine was then investigated as a CO₂ absorption rate promoter in aqueous MDEA in a stirred vessel with a plane horizontal gas-liquid interface. Benzylamine performed better than MEA and DEA as a rate promoting agent, a larger amount of benzylamine in aqueous MDEA resulting in a higher enhancement of CO₂ absorption rate.

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1. Introduction

The global energy demand is anticipated to double over the next 50 years. Nowadays coal is worldwide the major energy source and is likely to remain significant for the next decades. Carbon capture and sequestration (CCS) is a key technology for reducing CO₂ emissions for coal fired power plants. In CCS,

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CO₂ is separated from the flue gas, transported, and stored safely and permanently in underground geological structures.

Post-Combustion Capture (PCC) is the most mature technique for being implemented at large scale and can be retrofitted to existing power plants. In PCC, CO₂ is separated from the gas mixture after coal combustion. CO₂ in the flue gas is captured at low temperature by a selective chemical reaction between CO₂ and a solvent, typically aqueous alkanolamines. The CO₂-enriched solution is then pumped in a desorber where the chemical reaction is thermally reversed and CO₂ is released. No single amine delivers all process requirements such as low volatility and thermal and oxidative stability as well as energy efficiency.

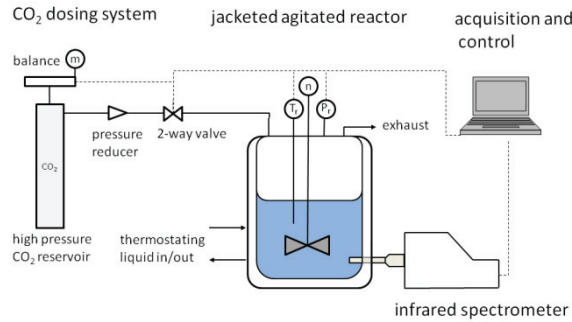
Amine blends are commonly used for acid gas treatment to combine the benefits of a fast reaction rate and a large absorption capacity. A typical composition consists of an aqueous mixture of a primary or secondary amine (e.g. monoethanolamine (MEA), diethanolamine (DEA), and piperazine (PZ)) and a sterically hindered or tertiary amine (e.g. 2-amino-2-methyl-1-propanol (AMP) and methyl-diethanolamine (MDEA)) [1,2,3].

To the best of our knowledge, investigations on aqueous benzylamine for acid gas treatment have never been published. Benzylamine has a primary amine functional group reacting relatively fast with carbon dioxide [4]. Ion-exchange beads functionalized with benzylamine are commercially available and used for efficiently capturing atmospheric CO₂ [5]. These beads were also reported to enhance CO₂ adsorption rate into aqueous MDEA when used as packing material in an absorption column [6].

In this study, we investigate the potential of aqueous benzylamine for capturing CO₂. First, CO₂ absorption capacity is measured in concentrated aqueous benzylamine and thermodynamic equilibrium constants are determined. Then, benzylamine is used as a rate promoter for CO₂ absorption in aqueous MDEA and compared to other promoters such as MEA and DEA.

2. Experimental

All the experiments were performed in a pressurised double wall stirred vessel (Parr) at constant temperature, T_r , as illustrated in Fig. 1. A known mass, m , of carbon dioxide (>99.9%, BOC Gases Australia) was introduced into the vessel partially filled with aqueous amine mixture as reported in Table 1 (MEA: monoethanolamine, ReagentPlus®, ≥ 99%), DEA: diethanolamine, 99%, MDEA: methyl diethanolamine, and BA: benzylamine, ReagentPlus®, 99%, all purchased from Sigma-Aldrich and used as received). The reactor pressure, P_r , was recorded to determine the amount of CO₂ in the gas phase [7] and, in turn, the amount absorbed by the solution. The stirring rate, n , (500 rpm) was chosen to maintain a plane horizontal gas-liquid interface and an efficient mixing. A 6mm ATR-FTIR probe connected to an iC10 spectrometer from Mettler Toledo via a K-6 mirrored conduit was used to monitor infrared spectra of the liquid phase during the absorption of CO₂. pKa of the solution was determined by titration following the experimental procedure given in [8].

Fig. 1. VLE apparatus with *in-situ* infrared monitoringTable 1. List of CO₂ absorption experiments with aqueous amine mixtures

Solvent (Amine 1)	Volume [ml]	Promoter (Amine 2)	Volume [ml]	V _{tot} [ml]	Amine 1 [% wt/wt]	C _{Amine 1} [M]	Amine 2 [% wt/wt]	C _{Amine 2} [M]
MDEA 30%	50	MEA	5	55	27.3	2.4	9.0	1.5
MDEA 30%	50	DEA	5	55	27.1	2.4	9.7	0.9
MDEA 30%	50	BA	5	55	27.4	2.4	8.8	0.8
MDEA 30%	50	BA	2.5	52.5	28.6	2.5	2.5	0.4
MDEA 30%	50	BA	1	51	29.4	2.6	1.9	0.2
MDEA 30%	50	--	--	50	30.0	2.6	--	--
BA 30%	50	--	--	50	30.0	2.8	--	--

The carbamate equilibrium constant was determined by a calibration-free spectroscopic method adapted from [9]. In short, a general chemical model was set as given in Table 2. $K_1 - K_3$ were taken from the literature and K_{prot} was measured by titration. Four additional mass balance equations (in terms of the CO₂, amine, proton, and hydroxide balance) were used allowing fitting of K_{carb} from the spectral data. IR absorbing species were HCO₃⁻, BA, BAH⁺ and BACOO⁻.

Table 2. Relevant equilibrium constants for modelling the reaction between benzylamine (BA), CO₂ and H₂O

Reaction	Equilibrium	Reference
$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$	$K_1 = \frac{[HCO_3^-]}{[H^+][CO_3^{2-}]}$	[10]
$H^+ + HCO_3^- \rightleftharpoons CO_2(aq) + H_2O$	$K_2 = \frac{[CO_2(aq)]}{[H^+][HCO_3^-]}$	[11]
$H^+ + OH^- \rightleftharpoons H_2O$	$K_3 = \frac{[H_2O]}{[H^+][OH^-]}$	[11]
$H^+ + BA \rightleftharpoons BAH^+$	$K_{prot} = \frac{[BAH^+]}{[H^+][BA]}$	this study
$BA + HCO_3^- \rightleftharpoons BACOO^- (+ H_2O)$	$K_{carb} = \frac{[BACOO^-]}{[HCO_3^-][BA]}$	this study

3. Results and discussion

3.1. CO₂ absorption in aqueous benzylamine

The absorption capacities of aqueous benzylamine (BA) 30% wt/wt at 40 °C, 60 °C, and 80 °C are presented and compared with MEA 30% in Fig. 1. At 15 kPa, the amount of CO₂ absorbed in BA is about 0.45 mol CO₂/mol BA, slightly lower than in MEA (~0.52 mol CO₂/mol MEA)[12]. The CO₂ loading drops to 0.3 mol CO₂/mol BA at 80 °C. While for a similar pressure BA absorbed less CO₂ than MEA, its cyclic CO₂ absorption capacity is higher. At 250 kPa CO₂ and 40 °C, carbamic acid salt precipitated [13,14]. No precipitate was observed at higher temperatures within the pressure range investigated in this study.

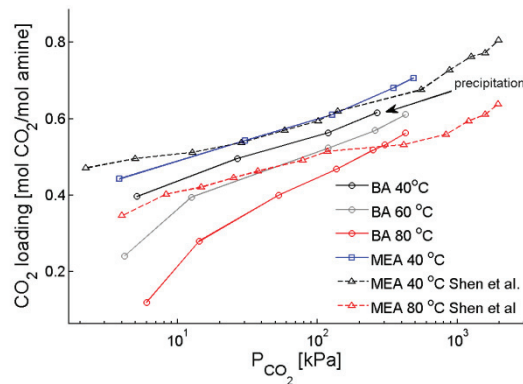


Fig. 2. CO₂ Vapour-liquid equilibrium data in benzylamine 30% wt/wt, at 40 °C, 60 °C, and 80 °C (circles). MEA 30% wt/wt is given for validation (squares) and comparison (triangle dashed lines) [12].

The amount of carbamate and bicarbonate is directly related to the absorption rate and the energy requirement for solvent regeneration. The protonation and carbamate equilibrium constants determined from titration and infrared experiments, respectively, are given in Table 3. Selected infrared spectra of aqueous BA under different CO₂ loadings as well as the protonated moiety are given in Fig. 4.

Table 3. Carbamate constant, K_{carb} , pKa, and standard molar enthalpy of protonation, ΔH_m° , of benzylamine (BA), monoethanolamine (MEA), and piperazine (PZ). The errors for the parameter values are the standard deviations calculated as part of the non-linear regression algorithm (K_{carb}) and the standard deviations of duplicate (pKa).

Temperature °C	$\log_{10} K_{carb}$		pKa			
	BA	MEA ref.	BA	BA ref.	MEA ref.	PZ ref.
25		1.31[15]	9.43±0.01	9.43[16], 9.33[17]	9.44[18]	9.73±0.02[19]
40	0.88±0.02	1.23[15]*	8.89±0.02	8.94[16]*	9.03[18]	9.39±0.05[19]
60	1.0±0.02	1.04[15]*	8.46±0.02			
80	0.93±0.02		7.71±0.07			* interpolated values
	ΔH_m° [J/mol]		-60.7		-41(2) [8]	-36(1)[8]

The carbamate stability constants, K_{carb} , of BA are slightly lower than for MEA meaning that less carbamate is formed (Table 3). K_{carb} changes little with temperature. Note that the value of K_{carb} at 40 °C should be carefully interpreted as the pressure range was limited due to precipitation. Thus, the concentration profiles of few species were linearly dependent such that the optimised value may be poorly defined [9].

The standard molar enthalpy of protonation, ΔH_m^o , gives direct information of the change of pKa with temperature, a greater change of pKa leading potentially to a lower process energy requirement. ΔH_m^o was calculated using a van't Hoff plot of $\ln K_{prot}$ against $1/T$ [8] ($pK_a = -\log_{10} K_{prot}$). As shown in Table 3, ΔH_m^o of benzylamine is greater than for MEA or PZ. The benzyl group on the carbon α of the primary amine may contribute to the rigidity of the structure and thus increases the exothermicity as observed with methyl substitution [8]. The greater pKa change with temperature may compensate for the stable carbamate and thus explain the higher cyclic absorption capacity of BA compared to MEA (Fig. 3).

3.2 CO₂ absorption in aqueous MDEA promoted by benzylamine

Benzylamine was then evaluated as a CO₂ absorption rate promoter in 30% wt/wt aqueous MDEA in a stirred vessel. Fig. 3 shows the evolution with time of the number of moles of CO₂ in the gas phase after dosing. The CO₂ absorption is clearly enhanced by addition of MEA and DEA, as reported in literature [3,20,21], as well as by benzylamine. Benzylamine shows the highest enhancement, the extend of which depends on its concentration (Fig. 3, right).

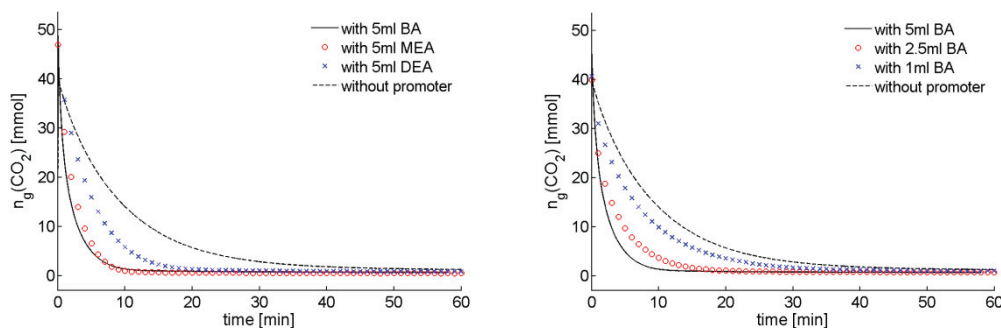


Fig. 4. Evolution of amount of CO₂ in the gas phase during the CO₂ absorption in 50 ml aqueous MDEA 30 % w/w promoted by MEA, DEA, and BA. The corresponding concentrations are given in Table 1.

A deeper understanding of the formation and consumption of the different species can be obtained by qualitative monitoring with *in-situ* infrared spectroscopy in the liquid phase [22,23]. IR spectra of aqueous MDEA and benzylamine under different CO₂ loading as well as under acidic conditions are given in Fig. 4. The typical bands of asymmetric stretching, $\nu_{as}(\text{COO}^-)$, at 1563 cm⁻¹ and the “umbrella” symmetric scissoring vibration, $\delta_s(\text{NH}_3^+)$, at 1524 cm⁻¹ are assigned to carbamate and protonated moieties of benzylamine, respectively. As MDEA is a tertiary amine, only the protonated moiety is formed that absorbs at 1076 cm⁻¹ due to $\nu_s(\text{C-N})$. 1356 cm⁻¹ and 1300 cm⁻¹ correspond to HCO₃⁻ stretching and scissoring, respectively [24].

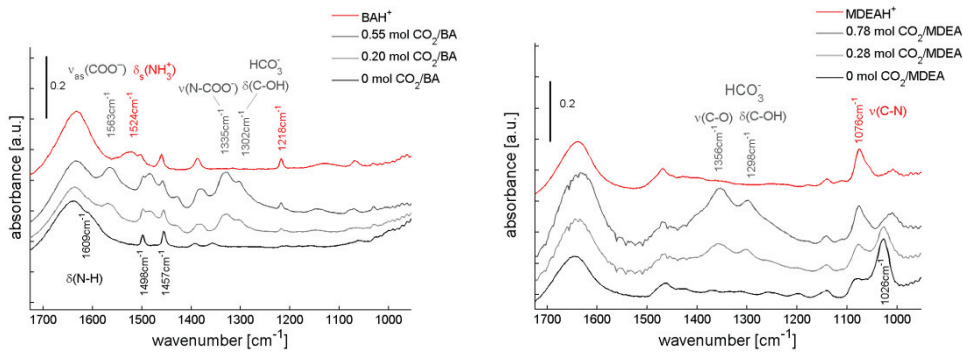


Fig. 5. Infrared spectra of protonated amines (red lines) and of CO₂-amine-H₂O (30% w/w) system under different CO₂ loadings (grey lines) in benzylamine (BA, left) and methyldiethanolamine (MDEA, right).

In the BA-MDEA mixture under different CO₂ loadings, BAH⁺ at 1524 cm⁻¹ is hardly detectable while specific absorption peaks of BACOO⁻, MDEAH⁺ and HCO₃⁻ are clearly observable (Fig. 5, left). As expected, the IR bands at 1076 cm⁻¹ (MDEAH⁺) and at 1302 cm⁻¹ (HCO₃⁻) increase much faster with addition of benzylamine than without (Fig. 5, right). Similarly, MDEA is consumed faster in the former case. MDEA acts as a pH buffer; it accepts the protons released by the reaction between benzylamine and CO₂ [25]. Consequently, benzylamine protonates in a rather small amount such that more free benzylamine is available for forming carbamate.

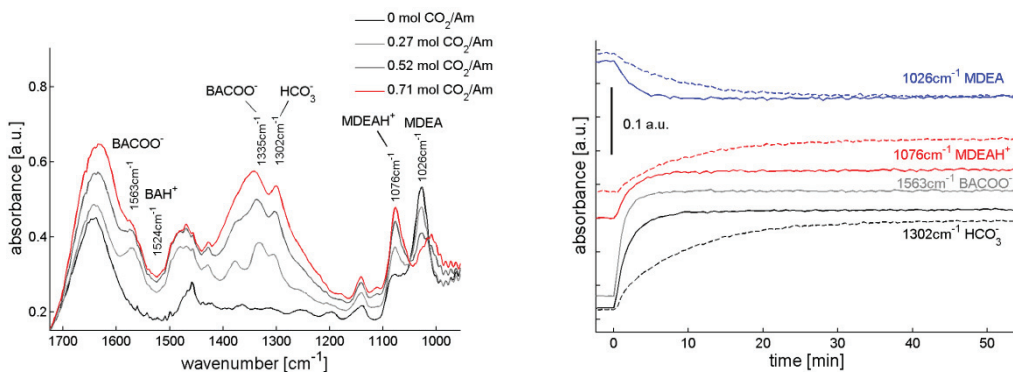


Fig. 6. CO₂ absorption in 50 ml aqueous MDEA with 5 ml BA. Left: IR spectra under different CO₂ loadings. Right: Evolution with time of selected IR bands during the absorption of CO₂ with and without benzylamine (solid and dashed lines, respectively). CO₂ was dosed in the vessel at t=0 min.

4. Conclusions

In this work it has been demonstrated that benzylamine is an attractive candidate for CO₂ post combustion capture from coal fired power station, especially if used as a rate promoter in an aqueous tertiary amine. The CO₂ loading capacity of 30 % wt/wt aqueous benzylamine between 40 °C and 80 °C under a pressure range up to 900 kPa has been investigated in a pressurised stirred vessel. At 40 °C and 250 kPa CO₂, carbamic acid salt precipitation was observed. The cyclic capacity was about 0.25 mol CO₂ per mol benzylamine. The protonation and carbamate thermodynamic equilibrium constants have been determined

and showed that benzylamine has a great change of pKa with temperature but forms rather stable carbamate moieties. Benzylamine was also investigated as a CO₂ absorption rate promoting agent in concentrated aqueous MDEA. Benzylamine showed a promoting effect greater than MEA or DEA.

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