EFFECT OF SULFATE AND NITRATE ANIONS ON THE CO_2 ABSORPTION PERFORMANCE OF AQUEOUS AMINE SOLUTIONS

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ABSTRACT

Solvent-based CO_2 capture is very important for the mitigation of greenhouse gases. The presence of SO_x and NO_x is observed in several types of CO_2-containing, industrial flue gases, where even small concentrations can cause changes in the performance of the solvent. The effects of SO_x and NO_x on monoethanolamine (MEA) and phase change solvents have been investigated to a limited extent, but no systematic study has been reported regarding their impact on the CO_2 solubility under different temperature and pressure conditions. The effect of SO_4^{-2} and NO_3^- in the CO_2 loading of aqueous MEA or of the aqueous phase-change solvent *N*-cyclohexyl-1,3-propanediamine (CHAP) – *N,N*-dimethylcyclohexylamine (DMCA) is investigated. The CO_2 solubility in 30.0% wt. aqueous MEA solutions containing 2.9% wt. H_2SO_4, as a source of SO_4^{-2}, and, in a subsequent experimental run, 1.8% wt. HNO_3, as a source of NO_3^-, is experimentally measured using a pressure decay method at 313, 333 and 353 K and 5-1000 kPa. Furthermore, the CO_2 solubility in 43.1% wt. aqueous DMCA+CHAP (3:1 mole ratio) solution containing 2.1% wt. H_2SO_4 is experimentally measured using a chemical analysis method at 313, 333 and 363 K and 10-100 kPa. For both solvent solutions, it was revealed that the addition of H_2SO_4 and/or HNO_3 does not alter the type of phase behavior (vapor-liquid or vapor-liquid-liquid equilibrium), but substantially decreases the CO_2 solubility.

KEYWORDS: CO_2 capture, sulfate and nitrate anions, MEA, DMCA, CO_2 solubility

INTRODUCTION

In a flue gas of a typical power plant the SO_2 content ranges between 500-3000 ppmv[1,2]. In general, wet SO_2 scrubbers are capable of removing 80–95% of the SO_2, while deep desulfurization (>99% purity) can have detrimental effects on the absorption process economics[3]. The maximum SO_2 levels that can be tolerated are 10 ppmv at the inlet of the monoethanolamine (MEA)-based CO_2 absorber[4]. Higher levels can create process problems, including foaming, corrosion, fouling, plugging, and solvent loss.

In the investigations that are reviewed below, quite often SO_2 is used in its gaseous form to perform the relevant experiments. When the SO_2 is absorbed in the aqueous phase, it produces HSO_3^- ions and this is often emulated using directly Na_2SO_3 solutions[5], instead of using the gaseous SO_2 which is much more difficult to handle. However, under realistic conditions the flue gases contain also O_2 and the liquid phase contains Fe cations due to corrosion. The produced HSO_3^- ions react with O_2 in a reaction that is catalyzed by Fe cations to produce SO_4^{-2} dissolved together with H^+ ions, i.e., the product of the dissolution of H_2SO_4[6]. The presence of the SO_4^{-2} ions is therefore unavoidable, hence it is important to investigate their effects on CO_2 capture systems as they represent part of a realistic liquid-phase composition in the absorber and desorber, instead of only having HSO_3^- ions.

Lepaumier et al.[7] have shown that amine degradation in CO_2 capture process is a very slow phenomenon and the high CO_2 pressure increases degradation rates without changing the reaction mechanisms. Supap et al.[8] have used experimental conditions which surpass the extremes normally encountered in a typical CO_2 capture process in a coal fired power plant. MEA concentration, O_2

concentration, SO_2 concentration, CO_2 concentration and degradation temperature were, respectively, in the range of $3 – 7$ $kmol/m^3$, $6 – 100\%$, $0 – 196$ ppm, $0 – 0.52$ loading, and 393K. In order to counter the detrimental amine effects of SO_2 and O_2, inhibitors were used. The blend of Na_2SO_3-$KNaC_4H_4O_6.4H_2O$ was the most effective inhibitor in CO_2 loaded or unloaded solutions.

Gao et al.[9] tested in a pilot plant the corrosion behavior of a blended amine absorbent specified by Toshiba using 200 ppm and 300 ppm SO_2. The results indicated that SO_2 is accumulated gradually in the solvent, and the SO_2 removal efficiency reaches almost 100%. The CO_2 removal efficiency gradually decreases as circulating time goes by, due to amine concentration decrease. Beyad et al.[10] showed that equilibrium and kinetic effects of accumulated SO_2 is negligible for low SO_2 concentration (0.3 M). If the concentration increases further, both equilibrium and kinetics cause a decrease of the cyclic capacity by 40% and a reduction of the CO_2 transformation kinetics by a factor of 2.

Bello and Idem[11] proposed many pathways for MEA oxidation. In loaded solutions, O_2 is produced as a degradation product, which implies that, on an oxidative degradation environment, oxygen could still be created. In addition, the oxidation of MEA solution increases upon loading. In continuation of their research, Uyanga and Idem[12] studied the effect of SO_2 in MEA loaded and unloaded solutions. They concluded that an increase in the concentrations of SO_2 and O_2 in the gas phase and monoethanolamine (MEA) in the liquid phase resulted in an increase in MEA degradation, whereas an increase in CO_2 loading in the liquid phase produced an inhibition effect to MEA degradation.

Voice and Rochelle[13] showed that dissolved metals and temperature are the two most important factors for MEA oxidation. Contamination by Fe^{+3} and Mn^+ from corrosion, fly ash, or other sources could cause up to a 3800% increase in the oxidation rate of MEA in the absorber. In addition, although higher loadings may benefit oxidation by decreasing the free MEA, they would increase thermal degradation[14].

The above review indicates that the combined use of SO_2 and O_2 is not investigated often and the influence of SO_4^{-2} is not elucidated sufficiently, despite its relevance to real capture systems operation. The lack of such ions is more pronounced in experiments that use pure SO_2 gaseous streams, where the absence of O_2 prohibits the appearance of SO_4^{-2}. It is also worth noting that most works pertain to MEA, but data are not presented systematically regarding the effects of SO_4^{-2} in the loading of MEA, compared to the loading of MEA without the presence of this contaminant. Systematic measurements of such data are important in order to enable the parameterization of appropriate thermodynamic models that can be used in the design of such systems. While MEA is a conventional solvent that exhibits vapor-liquid equilibrium, another type of solvents called phase-change solvents has received significant attention in recent years[15]. The latter solvents exhibit liquid-liquid phase separation upon a change in processing conditions and then they revert back to their single liquid phase once the original conditions are restored. The CO_2-rich phase of such a solvent includes a high concentration of the CO_2-adduct with some water, while the CO_2-lean phase comprises mainly amine and water and may be separated and returned to the absorber. This behavior enables significant energy and costs savings in the capture process, but it is quite complex and has not been investigated in the presence of either SO_2 or of its product SO_4^{-2} in published literature. Recently, Papadopoulos et al.[16] developed the novel phase-change solvent N-cyclohexyl-1,3-propanediamine (CHAP)/N,N-dimethylcyclohexylamine (DMCA), with excellent equilibrium behavior as well as technoeconomic performance[17]. However, all investigations were based on ideal flue gases that did not consider contaminants such as SO_4^{-2}.

In this work, we present systematic measurements of the vapor-liquid equilibrium behavior of MEA in the presence of SO_4^{-2} and we compare them with equilibrium data without this contaminant to highlight clearly its effects on the loading of MEA. We further present vapor-liquid-liquid equilibrium data for the novel phase-change solvent CHAP-DMCA in the presence of SO_4^{-2} and again compare its equilibrium behavior with data that do not include this contaminant. The presented data indicate

clear differences and are suitable for future direct use in the parameterization of predictive models that are of high relevance for scaling-up studies.

MATERIALS AND METHODS

The materials used in this work are shown in Table 1. They are used as received without further purification.

Table 1. Chemicals used in this work

Product Name	Abbreviation	CAS-numbers	Purity	Supplier
Carbon dioxide	CO_2	124-38-9	99.9 (vol%)	Air Liquide
Nitrogen	N_2	7727-37-9	99.9 (vol%)	Air Liquide
Sulfuric acid	H_2SO_4	7664-93-9	99%	Merck
Nitric acid	HNO_3	7697-37-2	65% or 70% in water	Merck
N,N-dimethylcyclohexylamine	DMCA	98-94-2	99%	Sigma Aldrich
N-cyclohexyl-1,3-propanediamine	CHAP	3312-60-5	98%	ITC
Monoethanolamine	MEA	141-43-5	99%	Thermoscientific

EXPERIMENTAL PROCEDURE

The CO_2 solubility in aqueous MEA+H_2SO_4(+HNO_3) solutions were measured using a pressure decay method and a relevant apparatus that is shown in Figure 1(a). The experimental procedure is described by Tzirakis et al.[23]. Briefly, the air is removed from the high pressure cell and, subsequently, a known amount of the aqueous solvent (around 25 g, maximum error ±0.002 g) is added. Then, 3-5 g of CO_2, depending on the experiment, are added to the system. The added amount of CO_2 is estimated (maximum error ±0.002 g) by measuring the mass (accuracy of ±0.001 g) of a high pressure CO_2 containing flask, before and after the addition. The pressure and the temperature inside the equilibrium cell are continuously monitored, using a pressure transducer (WIKA A-10, ± 0.5%) and a Pt-100 (± 0.01 K) thermometer, respectively. It is assumed that equilibrium conditions are reached upon pressure stabilization for at least 1 h. Knowing the temperature and pressure conditions, as well as the volume of the vapor phase, the amount of the absorbed CO_2 is calculated using the mass balance equations[23]. The equilibrium high-pressure cell is immersed inside a water bath of constant temperature (with temperature fluctuations as of 0.1 K). The volume of the cell (152.2 ± 1.6 cm³ at 298.15 K) was estimated at various temperatures by measuring the pressure after the addition of known CO_2 amounts. In all experimental conditions, the needed CO_2 densities were obtained from NIST[24]. According to such experimental procedure, the total pressure of the system is measured. In order to estimate the partial pressure of CO_2, the vapor pressure of the aqueous solution is subtracted from the total pressure. Since the investigated solutions are not volatile, such approximation, which is often used in similar studies[23,25], results in an insignificant correction, especially at relatively high pressures. In all cases, the uncertainties in the reported values for the CO_2 loading denote the maximum error, estimated through a propagation of errors analysis, knowing the uncertainties of all experimental measurements (i.e., weight of the materials, volume of the cell etc.)[23].

The CO_2 solubility in aqueous DMCA+CHAP+H_2SO_4 solutions was measured using a chemical analysis method. A simplified scheme of the experimental apparatus is presented in Figure 1(b). Pure CO_2 and mixtures of CO_2 and N_2 pass through a series of four gas wash bottles immersed in thermostatic water/oil bath. The first gas wash bottle contains de-ionized water in order to compensate vaporization losses. The second gas wash bottle is loaded with the aqueous amine solution. CO_2 partial pressures from 10 to 100 kPa were employed, over contact times of 2-5 hours, to ensure that equilibrium was achieved. When equilibrium is reached, samples of the one or two liquid phases are taken with a calibrated syringe for further analysis. Moreover, the compositions of the liquid phases in equilibrium (and consequently the CO_2 loading and the amine concentration) is ascertained by the barium chloride titration method and the total amine concentration by acid-base titration.
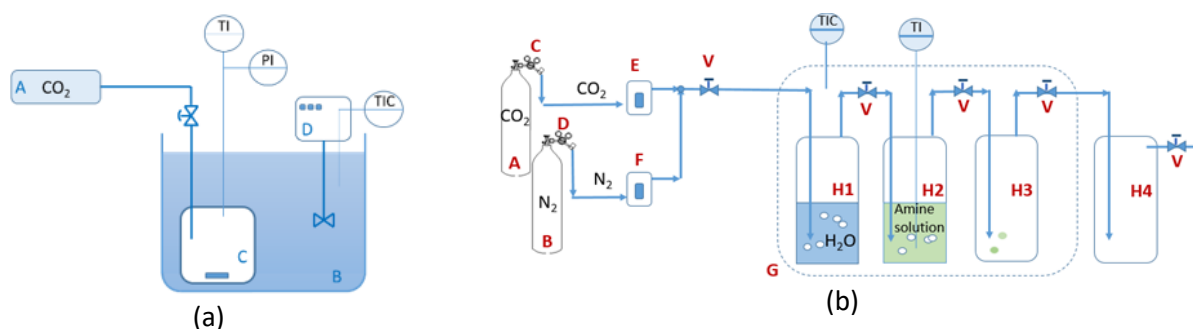
(a)　　　　　　　　　　　　　　　　　　　　　(b)

Figure 1(a). *Experimental apparatus for Vapor-Liquid equilibrium (VLE) measurements consisting of a CO_2 gas flask (A), water bath (B), equilibrium high-pressure cell (C), magnetically stirred and equipped with temperature and pressure sensors, and temperature controller (D)[23], (b) A simplified scheme of the experimental apparatus of the chemical analysis method: A: CO_2 tank, B: N_2 tank, C and D: Pressure Regulators, E: CO_2 Mass flow controller, F: N_2 Mass flow controller, H: Gas wash bottles (250 cm^3), G: Thermostatic bath, V: valves[15]*

RESULTS

CO₂ SOLUBILITY IN AQUEOUS MEA in solutions with H_2SO_4 and HNO_3

The experimental results in terms of loading, expressed as mole of CO_2 per mole of MEA, are presented in Figures 2(a,b,c).
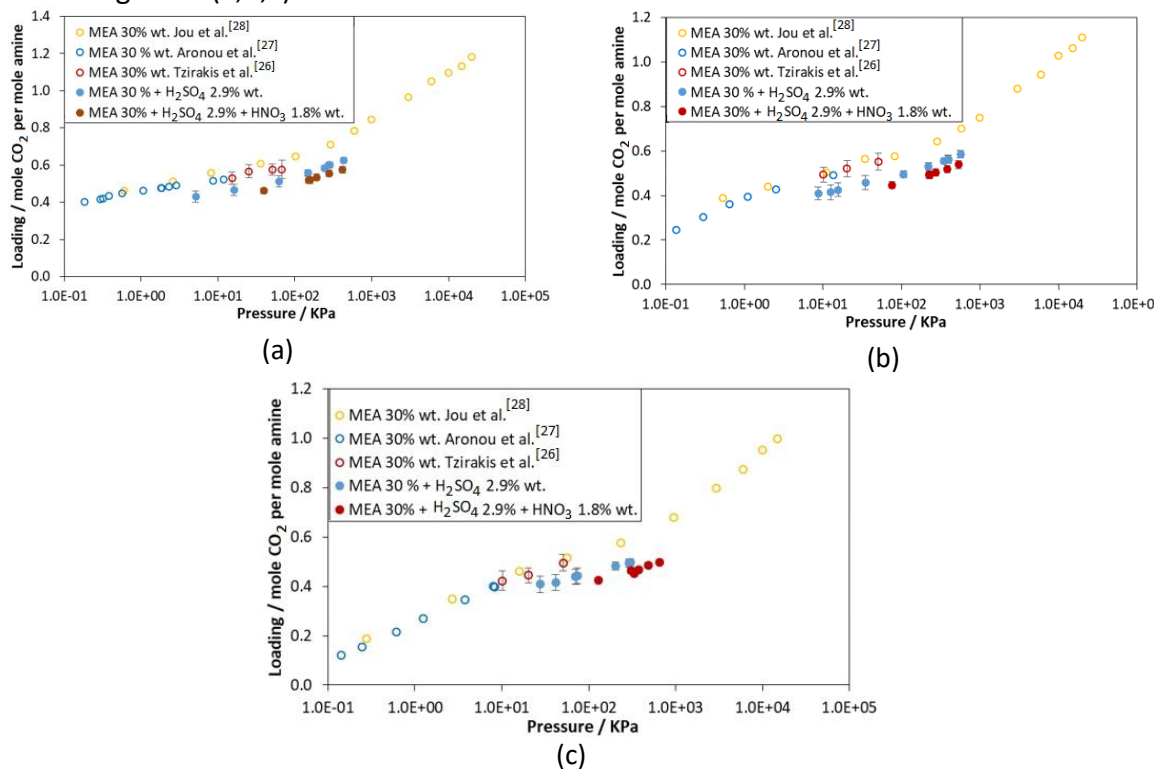

(a)　　　　　　　　　　　　　　　　　　　　　(b)

(c)

Figure 2 (a). *CO_2 loading of neat MEA (30% wt., red open circles from Tzirakis et al.[26], blue open circles from Aronou et al.[27] and yellow open circles from Jou et al.[28]), MEA+H_2SO_4 (30.0 + 2.9% wt., blue solid circles) and MEA+H_2SO_4+HNO_3 (30.0 + 2.9% + 1.8 % wt., red solid circles) aqueous solutions, at 313 K, (b). CO_2 loading of neat MEA (30% wt., red open circles from Tzirakis et al.[26], blue open circles from Aronou et al.[27] and yellow open circles from Jou et al.[28]), MEA+H_2SO_4 (30.0 + 2.9% wt., blue solid circles) and MEA+H_2SO_4+HNO_3 (30.0 + 2.9% + 1.8 % wt., red solid circles) aqueous solutions, at 333 K, (c). CO_2 loading of neat MEA (30% wt., red open circles from Tzirakis et al.[26], blue open circles from Aronou et al.[27] and yellow open circles from Jou et al.[28]), MEA+H_2SO_4 (30.0 + 2.9% wt., blue solid circles) and MEA+H_2SO_4+HNO_3 (30.0 + 2.9% + 1.8 % wt., red solid circles) aqueous solutions, at 353 K.*

The comparison of the new experimental data with that of neat MEA aqueous solutions reveals a significant decrease in CO_2 loading. For example, around 10-30 kPa of CO_2 partial pressure, a reduction of the CO_2 loading around 16% and 18% is observed at 313 and 333 K, respectively. Thus, the deterioration of solvent properties seems to increase with increasing temperature. However, it should be mentioned that the concentration of the added H_2SO_4 is high, higher than the expected concentration due to the dissolution of SO_2 in the liquid solvent and its subsequent transformation to sulfate anions in the presence of the O_2 that remains in the flue gas and Fe^{+3} acting as a catalyst. Thus, the used H_2SO_4 concentration simulates the accumulation of SO_4^{-2} inside an aged solvent. In addition, the existence in the solution of cations H^+ and anions NO_3^- from the addition of HNO_3 which simulates the dissolution and oxidation of nitrogen, leads to the binding of more amine according to reaction. This causes the even further decrease of CO_2 solubility.

CO_2 SOLUBILITY IN AQUEOUS DMCA+CHAP+H_2SO_4 SOLUTIONS

The experimental results in terms of loading, expressed as mole of CO_2 per mole of amine (DMCA+CHAP), are presented in Figures 3(a,b). It is observed that at low CO_2 partial pressures, the system presents Vapor-Liquid-Liquid equilibrium (VLLE) behavior, similarly to the DMCA or the DMCA-CHAP aqueous solutions. In more detail, at 313 K and 333 K, the system presents VLLE behavior for CO_2 partial pressures lower than approximately 25 kPa and 65 kPa, respectively, while it presents VLE behavior at higher CO_2 partial pressures.
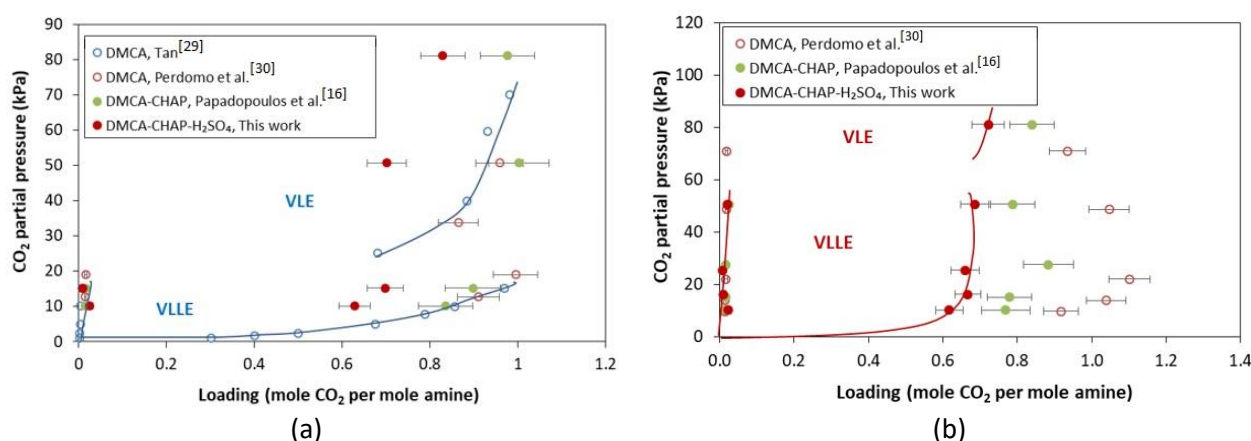

(a)   (b)

Figure 3 (a). *CO_2 loading of DMCA (3M) blue open circles from Tan [29], DMCA (3M) red open circles from Perdomo et al.[30], DMCA+CHAP (43% wt., 3:1 mol ratio) green solid circles from Papadopoulos et al.[16] and DMCA+CHAP+H_2SO_4 (43.1 + 2.1% wt., 3:1 mol ratio, red solid circles) aqueous solutions from this work, at 313 K, (b). CO_2 loading of DMCA (3M) red open circles from Perdomo et al [30], DMCA+CHAP (43% wt., 3:1 mol ratio) green solid circles from Papadopoulos et al.[16] and DMCA+CHAP+H_2SO_4 (43.1 + 2.1% wt., 3:1 mol ratio, red solid circles) aqueous solutions from this work, at 333 K.*

CONCLUSIONS

MEA in the regeneration column is not fully regenerated due to irreversible degradation of MEA when O_2, NO_2, and SO_x are present, which leads to various operational problems such as foaming, fouling, increased viscosity, and formation of heat-stable salts in the absorber that may not be regenerated. To examine further the detrimental acid effects on CO_2 capture, new experimental CO_2 solubility data were measured using MEA and DMCA+CHAP in conjunction with H_2SO_4 and HNO_3. It was revealed that the addition of H_2SO_4 does not alter the number of phases in equilibrium and, consequently, the CO_2 – aqueous MEA systems present VLE, while the CO_2 – aqueous DMCA/CHAP systems present VLLE at low CO_2 partial pressures. However, in both cases the addition of H_2SO_4 and HNO_3 considerably decreases CO_2 solubility in the aqueous liquid phases.

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