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**Citation for published version (APA):**

Mota Martinez, M., Samdani, S., Berrouk, A. S., Kroon, M. C., & Peters, C. J. (2014). Effect of additives on the CO<sub>2</sub> absorption in aqueous MDEA solutions. *Industrial and Engineering Chemistry Research*, 53(51), 20032-20035. <https://doi.org/10.1021/ie503915k>

**DOI:**

[10.1021/ie503915k](https://doi.org/10.1021/ie503915k)

**Document status and date:**

Published: 01/01/2014

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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# Effect of Additives on the CO<sub>2</sub> Absorption in Aqueous MDEA Solutions

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**S** Supporting Information

**ABSTRACT:** The use of antifoaming and corrosion inhibitor agents to prevent foaming and corrosion, respectively, is widely used in the carbon dioxide (CO<sub>2</sub>) absorption process using alkanolamines. However, the effect of these agents on the capacity of the alkanolamine solutions to absorb CO<sub>2</sub> is unknown. We present a study on the phase equilibria and solubility of CO<sub>2</sub> in mixtures of aqueous methyldiethanolamine (MDEA) solutions with and without these additives and show how the liquid phase properties and CO<sub>2</sub> loading capacity is affected.

## INTRODUCTION

The use of alkanolamines for CO<sub>2</sub> separation from natural gas is a technology that has been applied since the first patent was granted in 1931.<sup>1</sup> A wide variety of alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), di-2-propanolamine (DIPA) and *n*-methyldiethanolamine (MDEA) have been used.<sup>2</sup> The last one, MDEA, is usually preferred when large concentrations of hydrogen sulfide (H<sub>2</sub>S) are also present in the gas.

The first description of the use of MDEA in a process to selectively remove H<sub>2</sub>S in the presence of CO<sub>2</sub> is given in a publication by Frazier and Kohl.<sup>3</sup> Since then, numerous publications have been reported on the solubility of CO<sub>2</sub> and H<sub>2</sub>S in MDEA.<sup>4–8</sup>

Although the process for CO<sub>2</sub> capture with aqueous alkanolamines solutions is very mature, operating problems are still frequent. The most serious problem of alkanolamine processes is the corrosion, because it compromises not only operation effectiveness but also safety. In addition to selecting suitable equipment materials, corrosion inhibitors are often used during operation.<sup>9</sup>

Foaming is another major issue during operation of an absorption process using alkanolamines. Several causes for foaming formation have been identified, such as the presence of contaminants like liquid hydrocarbons, amine degradation products and other process chemicals including lubricant oil, corrosion inhibitors and suspended particles.<sup>10</sup> Foaming can be prevented by injection of antifoaming agents, which are usually silicones. They are added batch-like to the aqueous amine solution when needed.

The use of corrosion inhibitors and antifoaming agents is very common, but their effect on the CO<sub>2</sub> absorption is not clear and frequently disregarded. In this work, we have studied the effects on the solubility of CO<sub>2</sub> in aqueous MDEA (45.0 mass%) solutions, from a thermodynamic point of view, by addition of these agents.

## EXPERIMENTAL SECTION

**Materials.** The two antifoaming agents were SAG 7133 and VP 5371. SAG 7133 was received in an aqueous solution with 1 part of active component (polydimethylsiloxane) per 9 parts of water (10 mass%), whereas VP 5371 contained 2 parts of active component (organic silicone) per 8 parts of water (20 mass%). Both antifoaming agents were further diluted to 1.0 mass% in water. Therefore, 1 part of SAG 7133 was added to extra 9 parts of water and 1 part of the original VP 5371 solution was diluted in 19 parts of water.

Similar guidelines were followed to prepare the solution with the corrosion inhibitor CRO27005. The aqueous solution containing 1 part of active compound (benzotriazole) per 9 parts of water (10 mass%) was further diluted in 1 part of solution per 19 parts of water.

MDEA was added to the samples, so that in all cases, 45 parts of the amine were present per 55 parts of water.

**Experimental Procedure.** The effects of additives in MDEA were determined using a synthetic static method, in a so-called Cailletet apparatus. A schematic drawing and a detailed description of this facility can be found elsewhere.<sup>11</sup> The Cailletet apparatus can stand pressures up to 15 MPa and the operating temperature ranges from 275 to 370 K.

Each sample was prepared by placing a well-known amount of the liquid solution in a thick-walled Pyrex glass tube, also referred to as a Cailletet tube. Afterward, the tube was connected to a gas rack, the volume of which had been calibrated. The liquid sample was thoroughly degassed under vacuum conditions before dosing the desired amount of gas (CO<sub>2</sub> in this case). The temperature and pressure in the calibrated vessel was known, so the amount of moles of CO<sub>2</sub>

**Received:** October 3, 2014

**Revised:** November 27, 2014

**Accepted:** December 3, 2014

**Published:** December 3, 2014

could be calculated using the virial equation of state truncated after the second term. Mercury was used to push the gas into the Cailletet tube and to seal the sample in its closed top. Besides sealing the sample in the tube, mercury also acted as a pressure transmitting fluid.

The solubility of CO<sub>2</sub> in the amine solution has been determined following the bubble point pressure method. This method visually observes the disappearance of the CO<sub>2</sub> gas phase by gradually changing the temperature and/or the pressure of the system.

The pressure was generated by pressing hydraulic oil into the system with a screw type hand pump, which caused the level of the mercury column in the Cailletet tube to rise and to create the desired pressure on the sample in the top of the tube. A dead-weight pressure gauge was used to measure the pressure.

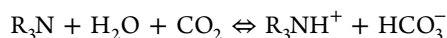
The temperature of the sample was kept constant by circulating a thermostat liquid through a thermostat jacket surrounding the Cailletet tube. In this work, water was used, so the temperature range was limited from 280 to 370 K. The temperature was measured with a platinum resistance thermometer in the heat jacket near the top of the sample tube. Homogeneous mixing of the sample was realized by moving a steel ball with two moving magnets.

The uncertainty in the measurements is  $\pm 0.005$  in the mole fraction of the composition,  $\pm 0.01$  K for the temperature measurements and the accuracy of the pressure gauge is  $\pm 0.01$  MPa.

## RESULTS AND DISCUSSION

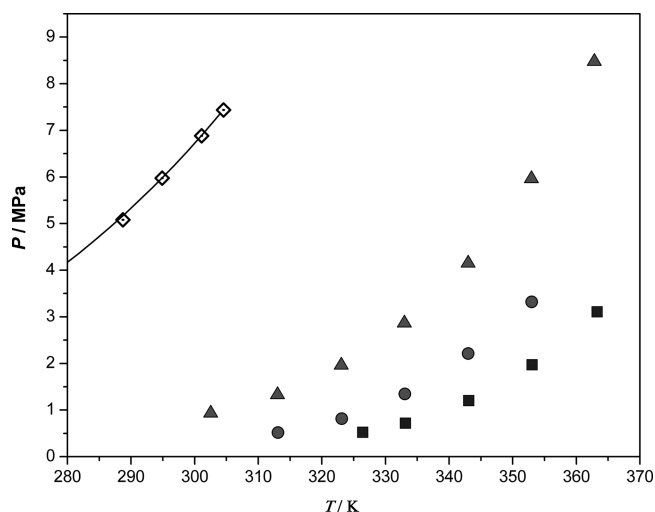
**Solubility of CO<sub>2</sub> in MDEA Solution.** The Cailletet apparatus has been used for numerous phase equilibrium and solubility studies, the majority of the systems being nonreactive. Although the high accuracy of this apparatus is unquestionable, the applicability to a reactive system was checked. Therefore, the solubility of CO<sub>2</sub> in a 45 mass% aqueous MDEA solution was determined and compared with literature data. Four isopleths (lines of constant composition) were measured at four different CO<sub>2</sub> loadings ( $\alpha = 0.8, 0.9, 1.0$  and  $1.5$  mol CO<sub>2</sub> per mole of pure MDEA).

The theoretical solubility limit for the absorption of CO<sub>2</sub> in the aqueous solution of MDEA is one mole of CO<sub>2</sub> per mole of MDEA ( $\alpha = 1.0$ ) according to the data and the chemical reaction model proposed by Jou et al.<sup>4</sup>

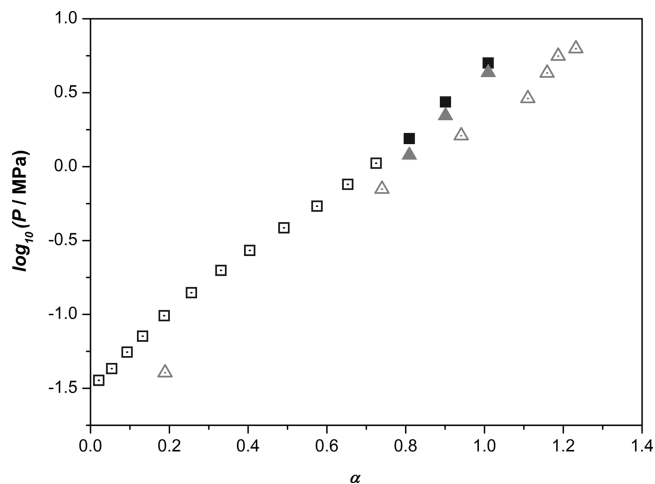


The results for the solubility of CO<sub>2</sub> in the 45% MDEA solution are summarized in Table S1 of the Supporting Information. Figure 1 shows that the samples with a CO<sub>2</sub> loadings ( $\alpha$ ) up to 1.0 present a vapor–liquid equilibrium (VLE) curve. As expected, only a vapor–liquid–liquid equilibrium (VLLE) was found for the  $\alpha = 1.5$  sample, meaning that the loading is beyond the solubility limit of CO<sub>2</sub> in the MDEA solution. This can also be noticed from the overlap of the experimental VLLE with the pure vapor pressure line of CO<sub>2</sub>.<sup>12</sup>

By fitting the measured isopleths to a third-order polynomial function, the isotherms at 343.15 and 348.06 K were calculated and compared to literature data,<sup>4,13</sup> as shown in Figure 2. The data reported in the literature at 343.15 K<sup>4</sup> have been used as reference data in handbooks,<sup>2</sup> although it has been claimed that the data of Sidi-Boumedine et al.<sup>13</sup> are more reproducible, less scattered and more reliable for modeling.<sup>14</sup> The reported values



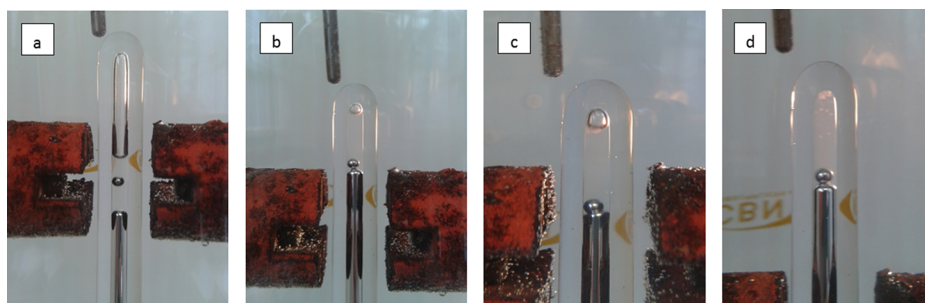
**Figure 1.** Experimental solubility of CO<sub>2</sub> in 45% MDEA solution. Composition is expressed in the ratio of moles of CO<sub>2</sub> per mole of MDEA:  $\alpha = 0.8$  (square symbol),  $\alpha = 0.9$  (circular symbol),  $\alpha = 1.0$  (triangular symbol) and  $\alpha = 1.5$  (diamond symbol). Closed symbols, VLE; open symbol, VLLE; solid line, VLE of pure CO<sub>2</sub>.<sup>12</sup>



**Figure 2.** Solubility of CO<sub>2</sub> in aqueous MDEA solution at 343.15 K (triangular symbol) and 348.06 K (square symbol). Solid symbols, this work. Open symbols, literature data at 343.15<sup>4</sup> and 348.06 K.<sup>13</sup>

at 348.06 K<sup>13</sup> were measured at lower pressures, even below the minimum pressure of the data measured in our system. Nevertheless, both sets of data clearly follow a similar trend, i.e. the data we measured with the Cailletet apparatus agree with literature data.

**Effect of Additives.** The effect of adding antifoaming agents and corrosion inhibitors on the solubility of CO<sub>2</sub> in aqueous solutions of MDEA was determined next. Figure 3 shows the evolution of the solution containing any of the antifoaming agents (SAG 7133 or VP 5371) in the Cailletet tube with increasing CO<sub>2</sub> pressure. At low pressure (Figure 3a), most of the CO<sub>2</sub> is in the vapor phase and the liquid is a homogeneous transparent mixture. As the sample is pressurized (Figure 3b), CO<sub>2</sub> starts dissolving in the liquid solution and a second gel-like liquid phase appears, which becomes more pronounced at higher pressures (near the bubble point), as shown in Figure 3c,d. Thus, at the given experimental conditions, CO<sub>2</sub> acts as an antisolvent for both antifoaming agents, causing the precipitation of a gel-like silicone-based



**Figure 3.** Effect of the CO<sub>2</sub> on the homogeneity of the liquid phase: (a) at low pressure, the CO<sub>2</sub> has not reacted yet, (b) the pressure is increased and the CO<sub>2</sub> starts reacting, (c) a second liquid phase is observed in the top of the Cailletet tube near the CO<sub>2</sub> bubble interface and (d) at high pressure, all the CO<sub>2</sub> has reacted and two liquid phases are observed.

substance from the liquid phase. Because antisolvation behavior of pressurized fluids are usually caused by physical interactions, it is expected that the interaction between CO<sub>2</sub> and the antifoaming agents is of physical nature.

To study if the precipitation was caused by the interaction of the antifoaming agent with CO<sub>2</sub> or simply a pressure effect, we prepared a sample with a loading of 0.1 mol of methane (CH<sub>4</sub>) per mole of MDEA in the aqueous solution containing the antifoaming agent VP 5371. The formation of the gel-like phase was not observed at any temperature–pressure condition up to 15 MPa. This proves that the interaction with CO<sub>2</sub> and not the pressure effect prompted the precipitation of the silicone-based antifoaming agent.

Precipitate formation did not occur upon addition of the corrosion inhibitor CRO27005 to the MDEA aqueous + CO<sub>2</sub> solution.

Measured results for the effect of adding antifoaming agents and corrosion inhibitors on the solubility of CO<sub>2</sub> in aqueous MDEA solutions at CO<sub>2</sub> loadings of 0.8 and 1.0 can be found in the Tables S2 and S3 of the Supporting Information. Figure 4 shows the bubble point pressure difference ( $\Delta P$ ) between the solutions of MDEA with and without the antifoaming agents or corrosion inhibitor for solutions of 0.8 and 1.0 CO<sub>2</sub> loading.

It has been found that the addition of any of the antifoaming agents increases the bubble point pressure and, as a consequence, the absorption of CO<sub>2</sub> in the aqueous amine

solution is negatively affected. On the basis of these data, we estimate that the CO<sub>2</sub> loading in the amine solution is reduced up to 2% when SAG 7133 is added and 1% when VP 5371 is present in the solution.

On the other hand, the solubility of CO<sub>2</sub> in the solution seems to be higher in the presence of the corrosion inhibitor agent CRO27005. Thus, unlike the antifoaming agents, the corrosion inhibitor decreased the bubble point pressure and increased the CO<sub>2</sub> absorption.

## CONCLUSIONS

The effect of adding the antifoaming agents SAG 7133 or VP 5371 and the corrosion inhibitor CRO27005 on the CO<sub>2</sub> absorption capacity of an aqueous MDEA solution (45%) was studied. It was established that the CO<sub>2</sub> acts as an antisolvent for both antifoaming agents and causes precipitation of the gel-like and silicone-based active agent. The solubility of CO<sub>2</sub> was negatively affected by the addition of both antifoaming agents, whereas the solubility increased when the corrosion inhibitor agent was used.

## ASSOCIATED CONTENT

### Supporting Information

Experimental bubble pressure data of CO<sub>2</sub> + aqueous MDEA solutions with/without additives. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

The paper was written through contributions of all authors. All authors have given approval to the final version of the paper.

### Funding

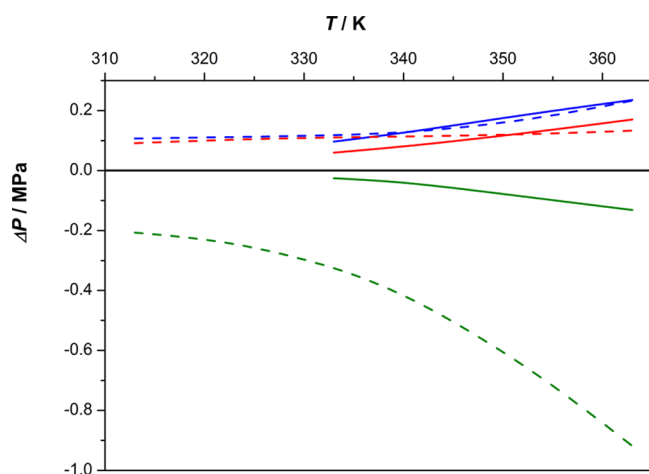
This work has been financed by the GASCO/ADGAS and the Gas Research Center of the Petroleum Institute in Abu Dhabi.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors acknowledge the Gas Subcommittee for supporting the project. Prof. Thijs Vlugt and M.Sc. Eugene Straver are especially acknowledged for permitting the use of the Thermolab at TU Delft and their guidance. Maria T. Mota-Martinez is grateful to the Petroleum Institute for the Visiting Graduate Researcher scholarship.



**Figure 4.** Effect of additives on the bubble pressure of aqueous MDEA solutions. Solid line,  $\alpha = 0.8$ ; dashed line,  $\alpha = 1.0$ . Blue line, solution with antifoaming agent SAG 7133; red line, solution with antifoaming agent VP 5371; green line, solution with corrosion inhibitor CRO27005.

## ■ ABBREVIATIONS

- $\alpha$  = CO<sub>2</sub> loading (moles of CO<sub>2</sub> per mole of MDEA)  
CH<sub>4</sub> = methane  
CO<sub>2</sub> = carbon dioxide  
DEA = diethanolamine  
DIPA = di-2-propanolamine  
H<sub>2</sub>S = hydrogen sulfide  
MDEA = N-methyldiethanolamine  
MEA = monoethanolamine  
VLE = vapor–liquid equilibrium  
VLLE = vapor–liquid–liquid equilibrium

## ■ REFERENCES

- (1) Bottoms, R. R. Process for separating acidic gases. U.S. Patent 1,834,016 A, Dec 1, 1931.
- (2) Kohl, A. L.; Nielsen, R. B. Alkanolamines for hydrogen sulfide and carbon dioxide removal. In *Gas Purification*, Fifth ed.; Kohl, A. L., Nielsen, R. B., Eds.; Gulf Professional Publishing: Houston, 1997; Chapter 2, pp 40–186.
- (3) Frazier, H. D.; Kohl, A. L. Selective absorption of hydrogen sulfide from gas streams. *Ind. Eng. Chem.* **1950**, *42* (11), 2288–2292.
- (4) Jou, F. Y.; Mather, A. E.; Otto, F. D. Solubility of hydrogen sulfide and carbon dioxide in aqueous methyldiethanolamine solutions. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21* (4), 539–544.
- (5) Austgen, D. M.; Rochelle, G. T.; Chen, C. C. Model of vapor-liquid equilibria for aqueous acid gas-alkanolamine systems. 2. Representation of hydrogen sulfide and carbon dioxide solubility in aqueous MDEA and carbon dioxide solubility in aqueous mixtures of MDEA with MEA or DEA. *Ind. Eng. Chem. Res.* **1991**, *30* (3), 543–555.
- (6) Jou, F.-Y.; Carroll, J. J.; Mather, A. E.; Otto, F. D. The solubility of carbon dioxide and hydrogen sulfide in a 35 wt% aqueous solution of methyldiethanolamine. *Can. J. Chem. Eng.* **1993**, *71* (2), 264–268.
- (7) Rho, S.-W.; Yoo, K.-P.; Lee, J. S.; Nam, S. C.; Son, J. E.; Min, B.-M. Solubility of CO<sub>2</sub> in aqueous methyldiethanolamine solutions. *J. Chem. Eng. Data* **1997**, *42* (6), 1161–1164.
- (8) Ma'mun, S.; Nilsen, R.; Svendsen, H. F.; Juliussen, O. Solubility of carbon dioxide in 30 mass % monoethanolamine and 50 mass % methyldiethanolamine solutions. *J. Chem. Eng. Data* **2005**, *50* (2), 630–634.
- (9) Zhao, B.; Sun, Y.; Yuan, Y.; Gao, J.; Wang, S.; Zhuo, Y.; Chen, C. Study on corrosion in CO<sub>2</sub> chemical absorption process using amine solution. *Energy Procedia* **2011**, *4* (1), 93–100.
- (10) Pauley, C. R. Face the facts about amine foaming. *Chem. Eng. Prog.* **1991**, *87* (7), 33–38.
- (11) De Loos, T. W.; Van der Kooi, H. J.; Ott, P. L. Vapor-liquid critical curve of the system ethane + 2-methylpropane. *J. Chem. Eng. Data* **1986**, *31* (2), 166–168.
- (12) Design Institute for Physical Properties. *DIPPR Project 801 - Full Version*; Design Institute for Physical Property Research/AIChE: New York, 2012.
- (13) Sidi-Boumedine, R.; Horstmann, S.; Fischer, K.; Provost, E.; Fürst, W.; Gmehling, J. Experimental determination of carbon dioxide solubility data in aqueous alkanolamine solutions. *Fluid Phase Equilib.* **2004**, *218* (1), 85–94.
- (14) Gabrielsen, J.; Michelsen, M. L.; Stenby, E. H.; Kontogeorgis, G. M. A model for estimating CO<sub>2</sub> solubility in aqueous alkanolamines. *Ind. Eng. Chem. Res.* **2005**, *44* (9), 3348–3354.