ELSEVIER

Advances in Gas Processing

Proceedings of the

4th International Gas Processing Symposium

26–27 October 2014
Doha, Qatar

Edited by:
Mohammed Jaber F. Al Marri | Fadwa T. Eljack

Proceedings of the 4th International Gas Processing Symposium

Advances in Gas Processing

Volume 1: Proceedings of the 1st Annual Gas Processing Symposium
edited by Hassan E. Alfadala, G.V. Rex Reklaitis and Mahmoud M. El-Halwagi

Volume 2: Proceedings of the 2nd Annual Gas Processing Symposium
edited by Farid Benyahia and Fadwa T. Eljack

Volume 3: Proceedings of the 3rd International Gas Processing Symposium
edited by Abdelwahab Aroussi and Farid Benyahia

Volume 4: Proceedings of the 4th International Gas Processing Symposium
edited by Mohammed Jaber F Al Marri and Fadwa T. Eljack

Proceedings of the 4th International Gas Processing Symposium

Edited by

Mohammed J. Al-Marri

Gas Processing Center, Qatar University
Doha, Qatar

Fadwa T. Eljack

Department of Chemical Engineering, Qatar University
Doha, Qatar

Amsterdam • Boston • Heidelberg • London • New York • Oxford
Paris • San Diego • San Francisco • Singapore • Sydney • Tokyo

Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN: 978-0-444-63461-0
ISSN: 1876-0146

List of Contents

Gas Conversion

Energy Mix

Operational Excellence

Environmental and Sustainability

Design and Modeling

This page intentionally left blank

Preface

Natural gas has been a valuable energy commodity for many centuries. Natural is considered the fastest growing segment of the energy market. The increased share of natural gas in the energy market is generally attributed to its low environmental impact and convenience in utilization as a fuel or feedstock in a wide range of petrochemical industry. It is also a key player in enhancing the efficiencies of power generation system. The challenge of energy security and environment requires solutions that are within reach; and natural gas is a flexible energy source that has the potential to complement emerging alternative technologies. Qatar is considered is one of the world's pioneers in implementing new processing technologies on a very large scale and accumulated a significant experience in operational excellence; and as such Qatar is positioned as one of the leading LNG and GTL exporters in the world.
The situation highlighted above lead to an inspired 4th international gas processing symposium covering the state-of-the-art advances in the area of natural gas utilization, sustainability and excellence in processing. The 4th international gas processing symposium held in Doha, Qatar from October 26 to 27, 2014.

A key future theme in the Symposium was Natural Gas and World's Energy Mix because of its growing importance of the global energy market. The Symposium also covered the following gas processing applications in parallel sessions:

- Environment Sustainability
- Carbon Management
- Energy Mix
- Gas Conversion Processes (GCP)
- Design & Modeling
- Operational Excellence I (OEI)
- Industrial Case Studies Session

The 4th international gas processing symposium combines an interesting variety of papers from academia and industry, giving a unique perspective into state of the art matters related to gas process which are presented in the chapters of this symposium proceedings book.

The organizing committee of the 4th international gas processing symposium wishes to express gratitude to people who made this event

possible and pleasant. Grateful acknowledgment is given to His Highness Sheikh Tamim bin Hamad AI-Thani, Emir of the State of Qatar. The support of her Excellency, Professor Misnad, President of Qatar University. The strong support of College of Engineering and the Gas processing Center staff at Qatar University is also gratefully acknowledged.

The organizing committee also wishes to extend their gratitude to the symposium sponsors: Qatar Petroleum, Dolphin Energy, OryxGTL, QAFAC, RasGas, ExxonMobil and professional partners: European Federation of Chemical Engineers (EFCE), Gas Processing Association (GPA)-GCC, American Institute of Chemical Engineers (AIChE), Elsevier (publisher), Industrial & Engineering Chemistry Research (I & EC Research)(Special Issue)

Finally, the editors would like to thank the authors who shared their knowledge and expertise in papers constituting the core content of this book.

Mohammed J. Al-Marri, Gas Processing Center, Qatar University, Qatar.

Fadwa T. Eljack, Department of Chemical Engineering, Qatar University, Qatar

Mohammed Jaber F. Al Marri and Fadwa El Jack (Editors), Proceedings of the 4th International Gas Processing Symposium, October 26–27, 2014, Doha, Qatar.

Solubility of CO_2 in aqueous amine solutions: a study to select solvents for carbon capture from natural-gas power plant

Jiafei Zhang[a], Danlu Tong[a,b], Paul S. Fennell[a,b], J. P. Martin Trusler[a,*]

[a]*Department of Chemical Engineering, Imperial College London, South Kensington Campus, Exhibition Road, London SW7 2AZ, United Kingdom*

[b]*Grantham Institute for Climate Change, Imperial College London, South Kensington Campus, Exhibition Road, London SW7 2AZ, United Kingdom*

** Email: m.trusler@imperial.ac.uk*

Abstract

New solvents or solvent formulations are required for the capture of CO_2 from natural gas power plants, the flue gases from which typically contain low concentrations of CO_2 coupled with relatively high concentrations of O_2. Information concerning vapour-liquid equilibrium, in particular CO_2 loading capacity, is important for the selection of solvents to be employed for absorption. A static-analytic apparatus has been developed to acquire such data at temperatures between (313 and 393) K and various CO_2 partial pressures. A tertiary amine, 2-dimethylaminoethanol (DMAE) and its blended solutions with piperazine (PZ) were studied. The density and viscosity of these amine solutions were also measured to yield a better understanding of their performance in mass transfer and fluid dynamics.

Keywords: CO_2 absorption, amines, vapour-liquid equilibrium, density, viscosity

1. Introduction

Anthropogenic CO_2 emissions from the combustion of fossil fuels have caused a significant increase in atmospheric greenhouse-gas concentrations and are beginning to change the global climate [1]. CO_2 capture and storage (CCS) is proposed as an intermediate solution to mitigate global warming and to allow continued use of fossil fuels. Amine-based CO_2 absorption has hitherto been the technology of choice for post-combustion capture (PCC) from fossil-fuel power stations, but challenges such as high energy consumption and solvent degradation still impede the implementation of conventional solvent scrubbing technologies for flue gas treatment [2-4]. The use of natural gas for power generation has greatly increased in recent years for both economic and environmental reasons. As shown in Table 1, the flue gas from natural gas power systems has a lower partial pressure of CO_2 (p_{CO_2}) and a higher concentration of O_2 compared to that from coal-fired power plant [5]. It is therefore necessary to select gas-specific solvents adapted for capturing CO_2 from natural gas combined cycle (NGCC) power plant. Such solvents should present a high CO_2 capacity at low p_{CO_2} and a good chemical stability, especially with regards to oxidative degradation.

Table 1. Typical flue gas compositions from coal and natural gas combustion

(unit: %)	**CO_2**	**N_2**	**O_2**	**H_2O**	**NO_x**	**SO_x**	**Ar**
Coal-fired	12-16	75-80	2-4	10-15	400 ppm	150 ppm	0.82
Gas-fired	3-5	70-75	10-12	7-10	<50 ppm	<10 ppm	0.89

2. Amines for CO_2 absorption

Amine solvents with their high capacity to absorb dilute CO_2 have been used commercially for gas sweetening. MEA is the most well-known alkanolamine and has been employed for the separation of acid gases in industrial processes for more than 80 years [6]. It is characterised by high absorption capacity, fast reaction kinetics, good aqueous miscibility and low cost. However, this solvent shows several disadvantages such as high energy requirement (3.5 to 4 GJ/ton-CO_2), solvent degradation, and corrosion issues. Therefore, it is essential to develop new amine solvents that meet the following criteria:

- Reduced energy consumption
- Fast reaction kinetics and high capacity with respect to CO_2
- Minimal environmental impact
- Low degradation and corrosivity

N-methyldiethanolamine (MDEA), as a tertiary amine, has been used for selective absorption of H_2S and CO_2 in many industrial processes [7]. Some MDEA-based solvents developed by Dow Chemicals were claimed to be more economic with regard to energy consumption than MEA-based solvents, primarily owing to the lower enthalpy of reaction [8]. MDEA also exhibits advantages of low volatility and excellent resistance against thermal and oxidative degradation. In addition, other tertiary amines *e.g.* 2-dimethylaminoethanol (DMAE) and 2-diethylaminoethanol (DEAE) were also proposed for PCC [9], but slow reaction kinetics prove to be one of the main shortcomings of this category.

Sterically hindered amines, *e.g.* 2-Amino-2-methyl-1-propanol (AMP), are considered as promising candidates for acid-gas scrubbing [10]. They present high CO_2 capacity and low degradability, but high vaporisation loss is a potential weakness. Other sterically hindered amines *e.g.* KS-1 commercialised by MHI [11] and 2-(isopropylamino)ethanol [12] were claimed to be superior compared to MEA in the PCC process.

Piperazine (PZ), a diamine with fast reaction kinetics, high CO_2 loading and good chemical stability, has also been recommended for PCC [13]. However, it has been mainly used as an absorption promoter in solvent formulations because of its limited aqueous solubility and high price. Additionally, other polyamines *e.g.* 2-(1-piperazinyl)-ethylamine (PZEA) [14] and Cansolv's proprietary solvent DC105 [15], have proved more effective for CO_2 capture from NGCC.

Blended amine solvents are proposed to combine the advantages of each component. The optimal recipe typically comprises a principal solvent with high net CO_2 capacity and an activator exhibiting fast reaction kinetics to improve the efficiency of both the absorption and regeneration processes. A successful example is activated MDEA (aMDEA) developed by BASF [16], which presents the merits of moderate energy requirement, excellent chemical stability and improved reactivity. In this work, we investigate two additional blended solvent systems: AMP+PZ and DMAE+PZ.

3. Experimental

A static-analytic apparatus, shown in Figure 1, has been employed for accurate VLE measurements on CO_2-amine-H_2O systems. The experiments were carried out in a 100 ml stainless steel vessel at various temperatures from (313 to 393) K and total pressures up to 1 MPa. Both the gas and liquid phases were analysed by a Perkin-Elmer Clarus 500 gas chromatograph (GC) to determine the coexisting-phase compositions. The apparatus was validated in

earlier work [17] but the GC analysis system with gas sampling valve was improved in this study.

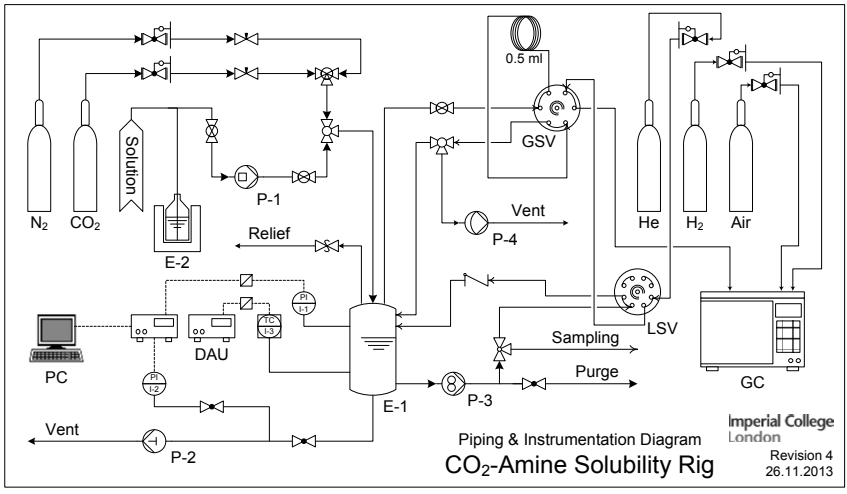

Figure 1. P&I Diagram of the static-analytic apparatus for VLE
DAU: data acquisition unit; E-1: jacketed reaction vessel; E-2: degasser; GC: gas chromatograph; GSV: gas sampling valve; LSV: liquid sampling valve; P-1: high pressure generator; P-2: rotary vane vacuum pump (0.01 kPa); P-3: gear pump; P-4: diaphragm vacuum pump (0.8 kPa); PC: computer.

MEA and PZ were purchased from VWR, and DMAE and AMP were supplied by Acros Organics. All of the tested amines were of at least 99 mass% purity. Aqueous amine solutions were prepared gravimetrically, and CO_2-saturated solutions were prepared from these by bubbling CO_2 through them at ambient pressure in a gas washing bottle. Partially loaded solutions were obtained by diluting CO_2-saturated solutions with fresh amine solution in the desired ratios. CO_2 loading ($\alpha_{\text{-}CO_2}$) was determined by GC analysis with an estimated uncertainty of 2%.

Density (ρ) was measured using an Anton Paar DMA 5000 M vibrating-tube densimeter in the temperature (T) range of (298 to 353) K. The uncertainty is estimated to be 0.05 kg/m^3. Kinematic viscosity (ν) was determined using a certified U-tube capillary viscometer (PSL) with an estimated uncertainty of 0.3%. Dynamic viscosity (μ) was calculated from the relation $\mu = \nu \cdot \rho$.

4. Vapour-Liquid Equilibrium

The apparatus was initially validated by measuring the solubility of CO_2 in 30 wt% aqueous MEA solution at temperature between (313 and 393) K. As shown in Figure 2, our results are in satisfactory agreement with the literature data of Jou *et al*. [18]. Further measurements were carried out for the tertiary amine DMAE and blended DMAE+PZ solutions. Figure 3 illustrates the good solubility of CO_2 in DMAE-based solutions at 313 K and excellent CO_2 regenerability at 393 K. The partial replacement of DMAE with PZ improves the CO_2 solubility slightly.

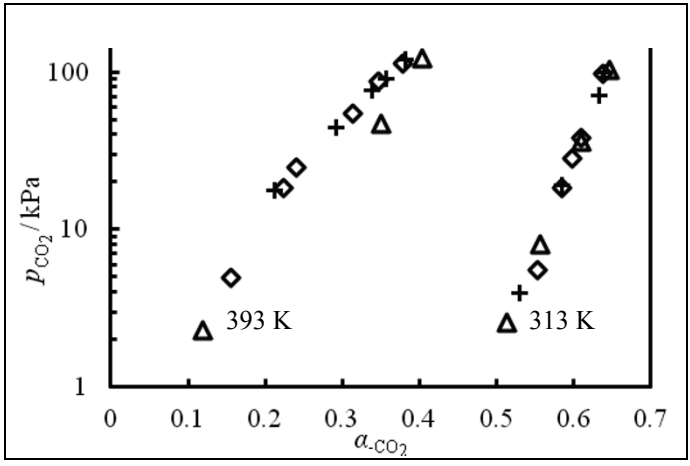

Figure 2. Solubility of CO_2 in 30 wt% MEA solution (◇ this work, + Tong *et al.*, 2012, Δ Jou *et al.*, 1995).

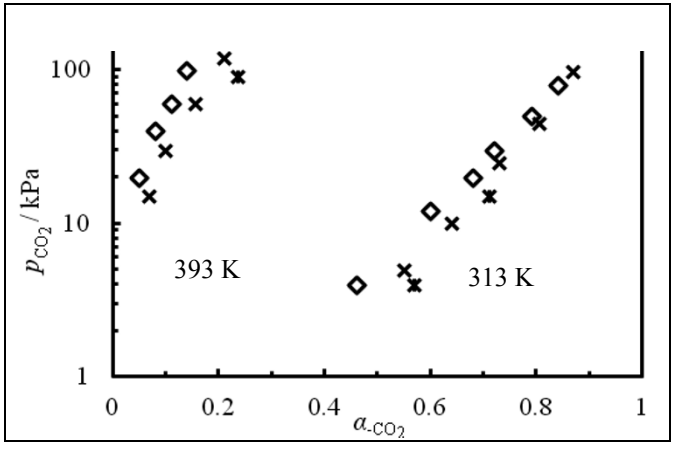

Figure 3. Solubility of CO_2 in 30 wt% DMAE (◇), 25 wt% DMAE+5 wt% PZ (×) and 20 wt% DMAE+10 wt% PZ (∗) solutions.

The cyclic loading capacity of CO_2 and alkalinity at low p_{CO_2} conditions were also studied to select specific amine solvents for NGCC-CCS. The proposed solvent formulations all have a higher net CO_2 capacity in comparison with the benchmark MEA and MDEA solvents (see Figure 4). Addition of the activator PZ in the solvent to replace part of the principle amine (AMP or DMAE) can not only accelerate the absorption rate but also improve the loading capacity, primarily due to the double amino function groups in a single molecule. Both the blended solvents AMP+PZ [19] and DMAE+PZ exhibit a good regenerability at the desorption condition.

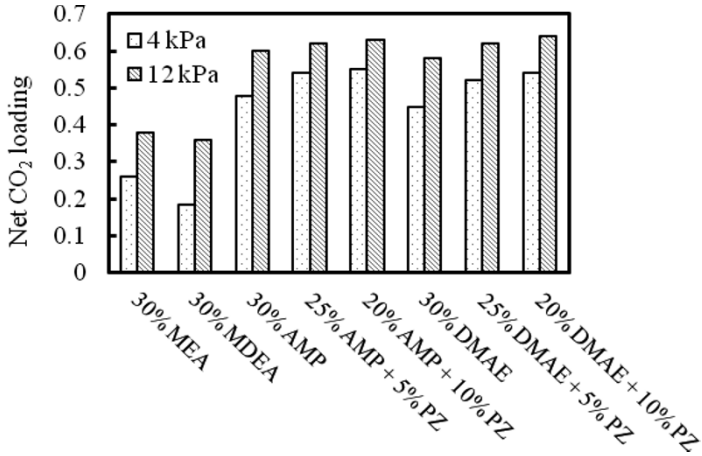

Figure 4. Comparison of net CO_2 capacity among the screened amine solvents.

5. Other thermophysical properties

To facilitate engineering calculations, it is essential to know the physical properties of solvents, and so properties such as the density and viscosity of aqueous amine solutions have been widely studied in the literature. However, very few literature data are available for CO_2-loaded aqueous amine systems. Our study therefore focuses on the effect of dissolved CO_2 on key thermophysical properties of aqueous amine solutions.

Density and viscosity are important for the process and plant design, especially relating to fluid dynamics calculations for the absorption column, gas-liquid mass transfer resistance and the selection of pumps and packings. The measurement systems were first validated with 30 wt% MEA solutions. As seen in Figure 5, the dynamic viscosity of MEA solutions is significantly increased by the dissolution of CO_2 and the measured data agree well with the values predicted from Weiland's correlation [20]. The maximum deviation is less than 3%.

Further measurements were conducted for DMAE and AMP solutions, and the effect of PZ addition and CO_2 loading was studied here. To suppress the temperature dependence of the data, the ratio of measured density ρ to the density of water (ρ_w) is presented in Figure 6, which illustrates that the ratio ρ/ρ_w is simply a linear function of T.

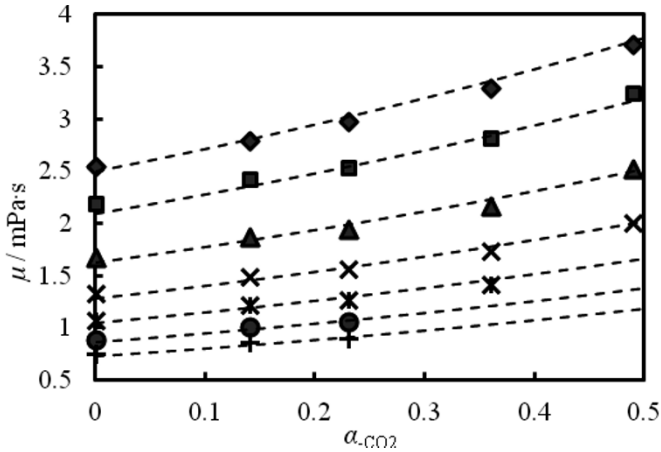

Figure 5. Dynamic viscosity of 30 wt% MEA solutions with various CO_2 loadings (◆ 298K, ■ 303K, ▲ 313K, ✕ 323K, ✳ 333K, ● 343K, + 353K, dashed lines: Weiland's correlation).

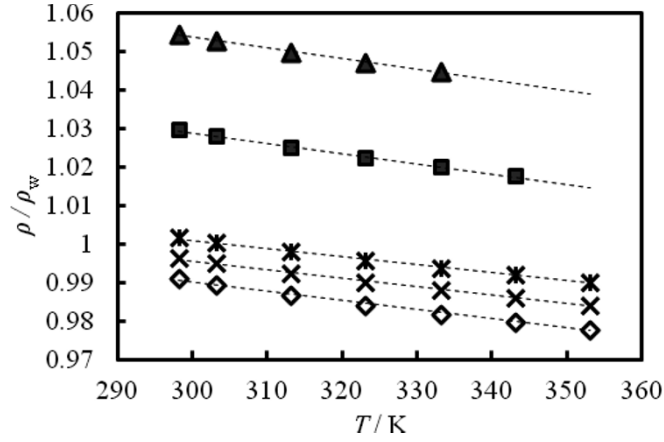

Figure 6. Density ratio of DMAE-based solutions to water with the influence of PZ addition and CO_2 dissolution (◇ 30 wt% DMAE, ■ 30 wt% DMAE + 0.8 mol/L CO_2, ▲ 30 wt% DMAE + 1.4 mol/L CO_2, ✕ 25 wt% DMAE + 5 wt% PZ, ✳ 20 wt% DMAE + 10 wt% PZ, dashed lines: linear fits).

The dynamic viscosity μ of 30 wt% DMAE, plotted in Figure 7, is much higher than the benchmark 30 wt% MEA. Both PZ addition and CO_2 loading enhance the viscosity, but the effect is quite weak in DMAE-based solutions. However, in the AMP-based solutions, μ is strongly enhanced by CO_2 dissolution (see Figure 8). In this case, both the DMAE- and AMP-based solutions can create a higher pressure drop along the absorption column compared to MEA; in addition, the packing at the bottom of the absorber should have a higher porosity than that at the top, since the viscosity of loaded AMP solution is almost double of that for the lean solution.

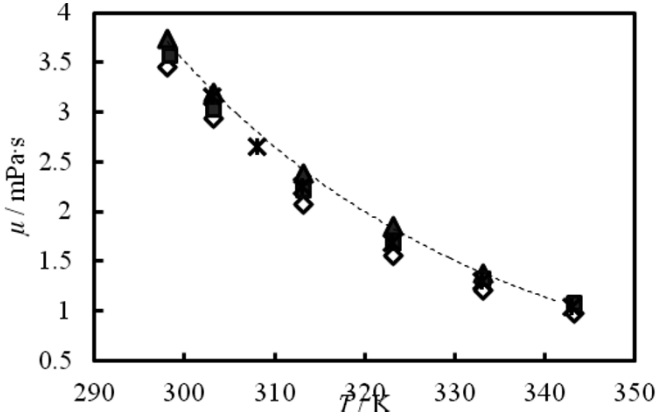

Figure 7. Dynamic viscosity of DMAE-based solutions (◇ 30 wt% DMAE, ■ 30 wt% DMAE + 0.8 mol/L CO_2, ▲ 30 wt% DMAE + 1.4 mol/L CO_2, ∗ 20 wt% DMAE + 10 wt% PZ, dashed line: exponential fit).

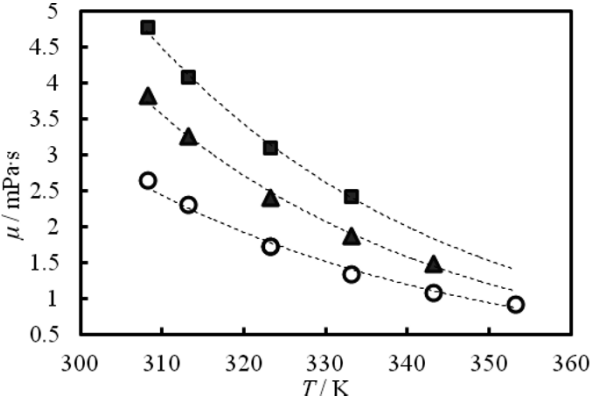

Figure 8. Dynamic viscosity of 20 wt% AMP+10 wt% PZ solutions (○ without CO_2, ▲ with 1.2 mol/L CO_2, ■ with 2.4 mol/L CO_2, dashed lines: exponential fits).