

Exploring Non-aqueous Solutions for CO₂ Capture at Elevated Pressure: An Initial Study for EHA/MOR in DMSO Mixtures

Mohd Azlan Kassim^{1*}, Zhongyi Ho², Farihahusnah Hussin², and Mohamed Kheireddine Aroua^{1,3}

¹Research Centre for Carbon Dioxide Capture and Utilisation (CCDCU), School of Engineering and Technology, Sunway University, No. 5 Jalan Universiti, Bandar Sunway, Petaling Jaya 47500, Selangor, Malaysia

²Department School of Engineering, Lancaster University, Lancaster LA1 4YW, UK

³Sunway Materials Smart Science & Engineering Research Cluster (SMS2E), Sunway University, No. 5 Jalan Universiti, Bandar Sunway, Petaling Jaya 47500, Selangor, Malaysia

Abstract. Carbon dioxide (CO₂) absorption in a non-aqueous solution is a potential technology for reducing greenhouse gas emissions. In this study, a non-aqueous solvent, dimethylsulfoxide (DMSO), was blended with amines. The non-aqueous blended amines absorbents' CO₂ absorption ability was investigated in a high-pressure absorption reactor with a variable absorption pressure (350–1400 kPa) at constant temperature (303.15K). The results showed that 2M EHA in DMSO solution had the highest CO₂ loading capacity (molCO₂/mol_{amine}) when compared with 1M EHA + 1M MOR in DMSO solutions. It was also found that the absorption capacity increased with increasing pressure. The highest CO₂ absorption by 2M EHA in DMSO solution was observed at a pressure of 1400 kPa at 303.15 K with 1.2507 molCO₂/mol_{amine}. The use of non-aqueous blended amine solvents showed no phase separation phenomenon after the CO₂ absorption reaction and the formation of carbamate salt was identified through FTIR analysis. 1 M EHA 1M MOR in DMSO has shown a higher initial absorption rate in comparison to 2 M EHA in DMSO which would suggest that the use of a 1M EHA + 1M MOR in DMSO as a non-aqueous solvent could be a promising solution for CO₂ capture.

1 Introduction

The combustion of fossil fuels and industrial processes primarily contribute to carbon dioxide (CO₂) emissions, leading to a range of environmental and health issues such as global warming, increased sea levels, and the proliferation of diseases. To combat this issue, absorption processes using aqueous alkanolamine solutions have been widely employed, but they suffer from problems such as corrosion, solvent loss, and high energy demands for regeneration [1, 2]. Recent research has highlighted the potential of organic solvents as alternatives to water in amine-based absorbents, offering benefits like lower regeneration

* Corresponding author: azlanka@sunway.edu.my

energy requirements and reduced corrosiveness [3]. This has spurred the need for innovative, environmentally friendly non-aqueous systems.

2-ethylhexylamine (EHA) is a promising candidate for efficient CO₂ capture due to its high absorption rate, but the steric hindrance of its amino group results in reduced stability of the absorption products and a lower desorption temperature [4], and morpholine (MOR), with its rapid reaction rate and thermal stability [5]. Additionally, dimethylsulfoxide (DMSO) has emerged as a versatile physical solvent with reduced energy consumption and non-corrosive properties [6]. These advancements in utilizing organic solvents and innovative absorbents promise to enhance CO₂ capture efficiency, reduce energy requirements, mitigate corrosion, and improve the overall environmental sustainability of CO₂ mitigation strategies [7]. In summary, the transition towards non-aqueous systems, incorporating EHA, MOR, and DMSO, presents a transformative opportunity to address the limitations of aqueous alkanolamine approaches in combating CO₂ emissions.

Therefore, this work focused on initial exploration on CO₂ absorption in non-aqueous mixture of EHA and MOR in DMSO at elevated pressure. CO₂ capacity and initial absorption rate will be evaluated along with the solvent density and FTIR analysis, pre- and post-carbonation. The work has potential to develop a non-aqueous solvent system with high CO₂ capacity and high CO₂ absorption rate.

2 Materials and Methods

2.1 Materials

Materials used in this work are: 2-ethylhexylamine (EHA), morpholine (MOR), and dimethylsulfoxide (DMSO) were purchased from Sigma-Aldrich. Carbon dioxide (CO₂) was purchased from Alpha Gas Solution. The chemicals were not subjected to any additional purification prior to their use.

2.2 Preparation of the non-aqueous blended amine mixtures

The 2 M EHA in DMSO and 1 M EHA + 1 M MOR in DMSO mixtures were prepared using a calibrated single-pan digital balance with a precision of 0.1 mg. The amount of EHA and MOR for each system concentration were calculated and weighed amounts of EHA and MOR were dissolved in DMSO to create non-aqueous solutions of mixed amines. The bottles containing the prepared mixtures were sealed tightly in order to prevent moisture from the surrounding atmosphere from being absorbed.

2.3 Evaluation of CO₂ absorption performance at elevated pressure

The evaluation of the non-aqueous solvent's efficiency in absorbing CO₂ was carried out according to the method outlined in prior research [8] and illustrated by Fig. 1. The experimental setup mainly consists of an air vent tube, a stirrer tank assembly, an inlet gas tube, and a thermocouple. The experiment is initiated by flushing CO₂ through the system to purge the air out of the gas reservoir. Once the system was purged, the gas reservoir is filled with pure CO₂ from the gas tank, subsequently, CO₂ is heated and pressurized into the required experimental conditions. The thermostated high-pressure reactor is filled with 20 ml of fresh solutions.

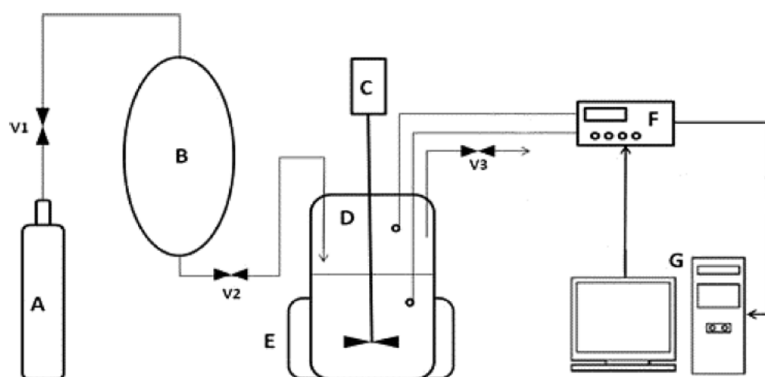


Fig. 1. Schematic diagram of high pressure CO₂ absorption set-up: A. Gas (CO₂) cylinder; B. Gas (CO₂) reservoir; C. Motor; D. High-pressure reactor vessel (equilibrium cell); E. Heater; F. Reactor controller; G. PC graphical user interface; V1. Control valve; V2. Needle valve; V3. Pressure relief valve.

2.4 Characterization of the non-aqueous mixtures

The 2M EHA in DMSO and 1M EHA + 1M MOR in DMSO mixtures were characterized by measuring their density at various temperatures. The density measurements were conducted using Anton Paar DMA 4200 M, at a temperature of 298.15 - 353.15 K and ambient pressure. The systems were further characterized using FTIR from 400 to 4000 cm⁻¹ wavenumber to identify the functional groups.

3 Results and Discussion

3.1 CO₂ Absorption in Non-Aqueous Solutions

The evaluation of CO₂ loading at an elevated pressure was conducted by adjusting the partial pressure from 350 to 1400 kPa, while maintaining a constant temperature of 303.15 K. Fig. 2 shows the CO₂ loading of the studied non-aqueous solvent mixtures. In general, the CO₂ loading of the studied non-aqueous amine-blended solvent mixtures increased with increasing partial pressure. The increasing pattern of CO₂ uptake with increasing pressure can be best represented by Le Chatelier's principle. The higher the concentration of CO₂ molecules in the gas phase, the greater the shift towards a new equilibrium state in which a larger amount of CO₂ is absorbed to counteract the influence of the partial pressure of CO₂ [8]. From Fig. 2, the result shows that 2M EHA in DMSO has a higher CO₂ loading in comparison to 1M EHA + 1M MOR in DMSO throughout the pressure studied. The loading difference may be attributable to the greater physical solubility of CO₂ in EHA versus MOR, which can be ascribed to the influence of the amines' molecular structure. The relationship between the amine's structure and its physical solubility is expected to be significant. As the steric hindrance in the amine structure increases, the solution becomes more bulky, leaving less "free" volume available for dissolving the gas [9, 10].

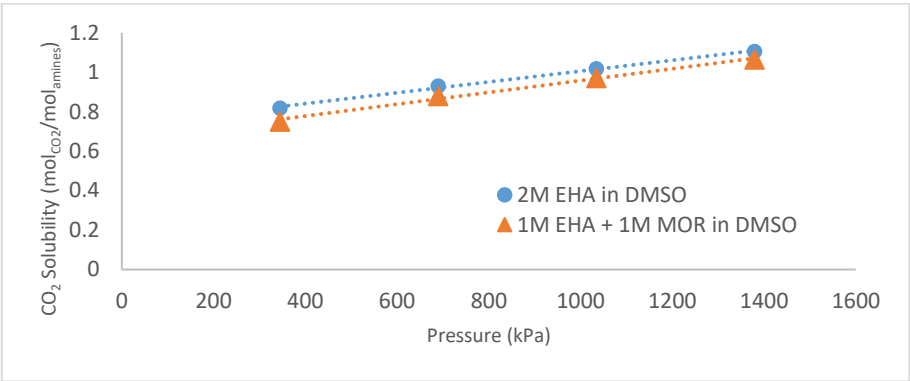


Fig. 2. Absorption of CO₂ into 2M EHA in DMSO and 1M EHA + 1M MOR in DMSO solutions at temperature of 303.15 K and various pressures.

3.2 Initial absorption rate

Fig. 3 shows the initial CO₂ absorption rate of two non-aqueous mixtures: 2M EHA in DMSO and 1M EHA + 1M MOR in DMSO. The initial CO₂ absorption rate refers to the rate at which the mixture absorbs carbon dioxide during the initial few seconds of exposure to the sample which was determined by analyzing the curve of the amount of CO₂ removed from the gas over time. This value was obtained using the initial slope method. The figure shows that the initial CO₂ absorption rate of 1M EHA + 1M MOR in DMSO is higher than that of 2M EHA in DMSO. This suggests that 1M EHA + 1M MOR in DMSO is more effective at absorbing CO₂ than 2M EHA in DMSO. The difference in initial CO₂ absorption rate between the two mixtures is likely due to the higher affinity of MOR for CO₂ than EHA. Upon carbonation, MOR forms a stronger carbamate bond in comparison to the linear EHA, leading to a higher CO₂ absorption rate in comparison to EHA [5].

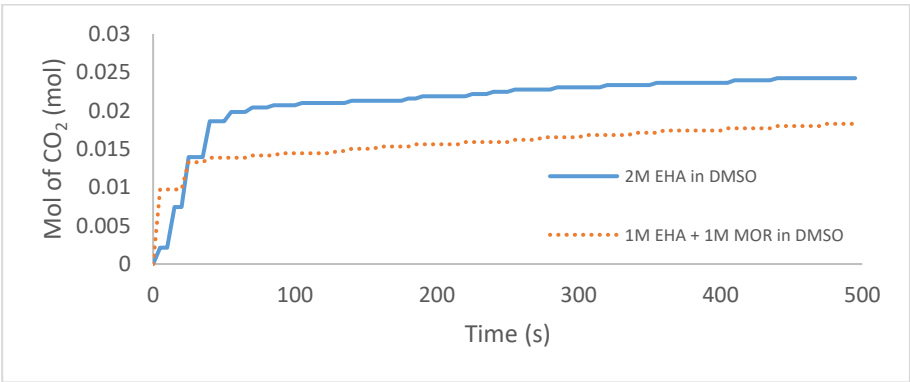


Fig. 3. Initial absorption rate of 2M EHA in DMSO and 1M EHA + 1M MOR in DMSO at 303.15 K and 350 kPa initial pressure.

3.3 Characterization of the non-aqueous mixture

3.3.1 Density

Fig. 4 illustrates the relationship between density and temperature in a non-aqueous mixture system (2M EHA in DMSO and 1M EHA + 1M MOR in DMSO) in comparison to the pure DMSO as a based solvent. The densities of the non-aqueous systems were determined at temperatures ranging from 298.15 K to 353.15 K and at ambient pressure. The precision of the density measurements was within $\pm 0.00001 \text{ g.cm}^{-3}$. All pure and mixture solvent systems measured show decreases in density with the increase in temperature. This demonstrates that as temperature rises, the kinetic energy of molecules also increases, resulting in reduced molecular interactions. Consequently, this causes an expansion in volume, leading to a decrease in density.

Experimental density data shows that density decreased when adding amines (EHA or/and MOR) into the based solvent, DMSO. The result shows that pure EHA has the lowest density followed by pure MOR and DMSO. Subsequently, upon mixing, the 2M EHA in DMSO solution has the lowest density in comparison to the 1M EHA + 1M MOR in DMSO solution at all temperatures. The decrease in density from the pure DMSO is due to the breakage and rearrangement of the DMSO intramolecular bond with the introduction of EHA or MOR into the solution [11].

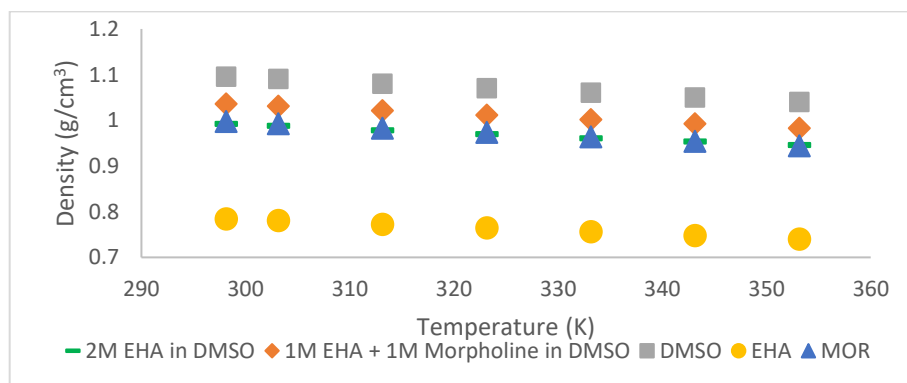
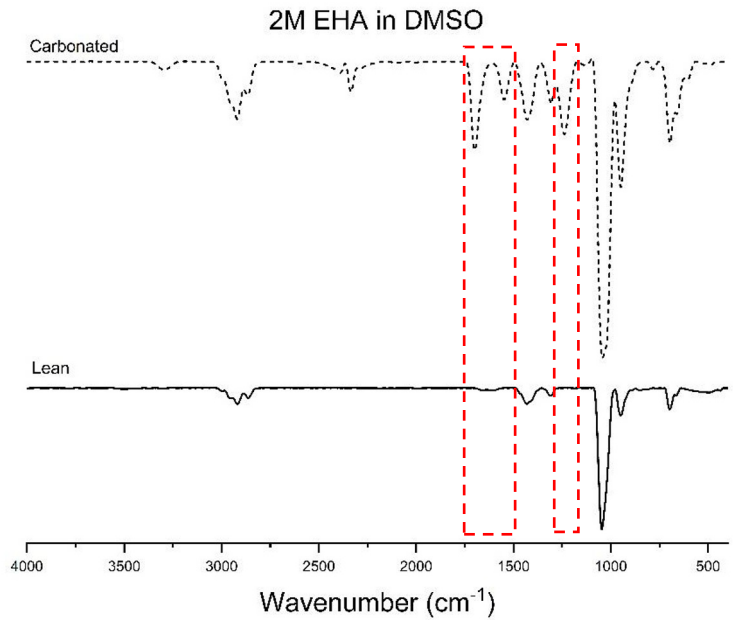


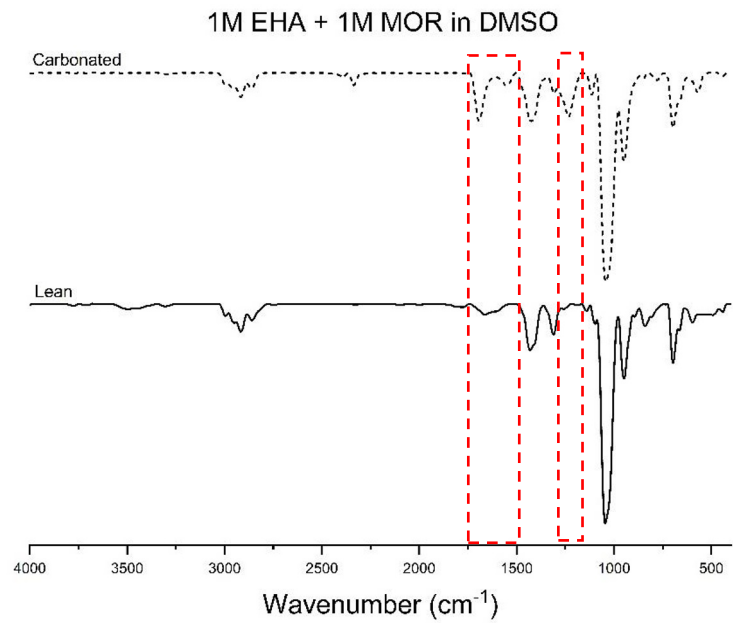
Fig. 4. Density of pure and non-aqueous amines mixtures at $T = 298.15 - 353.15 \text{ K}$.

3.3.2 Fourier transform infrared (FTIR) analysis

Fig. 5 (a and b) illustrates the FTIR spectra for 2M EHA in DMSO and 1M EHA + 1M MOR in DMSO before and after CO_2 absorption. The spectra illustrates the presence of carbonate peaks that reflect the formation of the carbamate salt of EHA in DMSO after absorption of CO_2 , 1699, 1548, and 1239 cm^{-1} , respectively. Similarly, the spectra show the presence of carbonate peaks that reflect the formation of carbamate salt of EHA and MOR in DMSO after absorption of CO_2 , 1692, 1551, and 1233 cm^{-1} , respectively. The presence of these peaks can be ascribed to the nitrogen atom that is bonded to the imide groups, suggesting that a reaction between carbon dioxide (CO_2) and the nitrogen atom connected to the carbonyl group (C=O) within the amide group has taken place. [12].



(a)



(b)

Fig. 5. FTIR spectra of lean and carbonated non-aqueous blended amine solutions; (a) 2M EHA in DMSO, (b) 1M EHA + 1M MOR in DMSO.

4 Conclusion

In the present study, initial measurements of the CO₂ loading for a non-aqueous blended amine mixture of EDA and MOR in a DMSO system were conducted at elevated pressure at a constant temperature of 303.15 K. The CO₂ solubility increase as the partial pressure was raised from 350 to 1400 kPa for all the non-aqueous blended amine samples that were prepared. Despite 2M EHA in DMSO having a higher CO₂ loading in comparison to 1M EHA + 1M MOR in DMSO throughout the pressure studied, 1M EHA + 1M MOR in DMSO have a higher CO₂ initial absorption rate in comparison to 2M EHA in DMSO measured at 303.15 K and 350 kPa initial pressure. The results indicate that the combination of 1M EHA and 1M MOR in DMSO as a non-aqueous blended amine solvent presents a promising approach for CO₂ capture. Pre-carbonation density of the non-aqueous mixtures was successfully measured with showed a decrease in density with the introduction of amine with DMSO. FTIR analysis was conducted to confirm the present of carbamate formation post-carbonation. Further research is required to assess the extent to which the non-aqueous amine solvent system performs in real-world settings and to identify the best conditions for operation.

The author would like to extend their gratitude to Sunway University for awarding this project under the Internal Grant Scheme (IGS) 2023 (GRTIN-IGS(02)-CCDCU-07-2023).

References

1. Gu, Y., Y. Hou, S. Ren, Y. Sun, and W. Wu, *Hydrophobic Functional Deep Eutectic Solvents Used for Efficient and Reversible Capture of CO₂*. ACS Omega, 2020. **5**(12): p. 6809-6816.
2. Chen, C.-C., Y.-H. Huang, S.-M. Hung, C. Chen, C.-W. Lin, and H.-H. Yang, *Hydrophobic deep eutectic solvents as attractive media for low-concentration hydrophobic VOC capture*. Chemical Engineering Journal, 2021. **424**: p. 130420.
3. Heldebrant, D.J., P.K. Koech, V.-A. Glezakou, R. Rousseau, D. Malhotra, and D.C. Cantu, *Water-Lean Solvents for Post-Combustion CO₂ Capture: Fundamentals, Uncertainties, Opportunities, and Outlook*. Chemical Reviews, 2017. **117**(14): p. 9594-9624.
4. Fu, K., M. Zheng, and D. Fu, *Low partial pressure CO₂ capture in packed tower by EHA+Diglyme water-lean absorbent*. Energy, 2023. **266**: p. 126530.
5. Mazari, S.A., R. Abro, A.W. Bhutto, I.M. Saeed, B.S. Ali, B.M. Jan, L. Ghalib, M. Ahmed, and N.M. Mubarak, *Thermal degradation kinetics of morpholine for carbon dioxide capture*. Journal of Environmental Chemical Engineering, 2020. **8**(3): p. 103814.
6. Kant, V., B.L. Jangir, and V. Kumar, *Gross and histopathological effects of dimethyl sulfoxide on wound healing in rats*. Wound Medicine, 2020. **30**: p. 100194.
7. Zhou, X., C. Liu, Y. Fan, L. Zhang, S. Tang, S. Mo, Y. Zhu, and Z. Zhu, *Energy-efficient carbon dioxide capture using a novel low-viscous secondary amine-based nonaqueous biphasic solvent: Performance, mechanism, and thermodynamics*. Energy, 2022. **255**: p. 124570.
8. Kassim, M.A., N.A. Sulaiman, R. Yusoff, and M.K. Aroua *Non-Aqueous Solvent Mixtures for CO₂ Capture: Choline Hydroxide-Based Deep Eutectic Solvents Absorbent Performance at Various Temperatures and Pressures*. Sustainability, 2023. **15**, DOI: 10.3390/su15129191.

9. Han, S.-J. and J.-H. Wee, *Estimation of the Amount of CO₂ Chemically Absorbed in Real Time by Measuring the Electrical Conductivity Variation of Monoethanol-Amine Aqueous Solutions*. Energy & Fuels, 2023. **37**(24): p. 19715-19725.
10. El-Naas, M.H., Z.M. Ismail, and M.H. Al-Marzouqi, *Correlating the physical solubility of CO₂ in several amines to the concentrations of amine groups*. Journal of Natural Gas Science and Engineering, 2016. **34**: p. 841-848.
11. Dubey, G.P. and R. Singh, *Influence of alkyl chain length and temperature on the densities, viscosities and speeds of sound of binary liquid mixtures of {2-methyl-1-butanol + 2-ethoxyethanol, or 2-propoxyethanol, or 2-butoxyethanol} at T = (298.15, 303.15 and 308.15) K*. The Journal of Chemical Thermodynamics, 2023. **184**: p. 107070.
12. Mohamed Mohsin, H., A. Mohd Shariff, and K. Johari, *3-Dimethylaminopropylamine (DMAPA) mixed with glycine (GLY) as an absorbent for carbon dioxide capture and subsequent utilization*. Separation and Purification Technology, 2019. **222**: p. 297-308.