Density, Viscosity, and Physical CO\textsubscript{2} Diffusivity of Novel Formulated Solvent N-Methyl-4-Piperidinol and 2-Amino-2-Methyl-1-Propanol for Carbon Capture

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Abstract—Amine based CO\textsubscript{2} capture is considered as one of the most effective technologies for mitigating global warming and climate change problems. The key of this technology is to use as highly effective solvent. In the present work, novel formulated MPDL-AMP solvent has been firstly introduced. Its essential data for determining and investigating the solvent performance as an alternative solvent for capturing CO\textsubscript{2} has not yet been reported. Therefore, density, viscosity, and physical CO\textsubscript{2} diffusivity of novel formulated MPDL-AMP solvent were determined in this work over ranges of concentrations and temperatures of 25\%wt., MPDL/5\%wt. AMP to 15\%wt. MPDL/15\%wt. AMP and 313 K to 333 K, respectively. The physical data reported in the present work are important for determining the optimum hydrodynamics of the fluid flow inside the absorption column as well as designing the height of the column through the kinetics and the mass transfer data. The results observed in the present work showed that the novel formulated MPDL-AMP solvent should be further investigated for its potential to be used as an alternative solvent for capturing CO\textsubscript{2}.

Index Terms—Amine, CO\textsubscript{2} density, diffusivity, viscosity.

I. INTRODUCTION

It is well known that carbon dioxide (CO\textsubscript{2}) is the major greenhouse gas (GHG) responsible for global warming and climate change problems. In order to reduce the CO\textsubscript{2} emission from large point industrial source, carbon capture technology should be implemented. One of the very most promising and successful methods is amine based CO\textsubscript{2} absorption [1]. This statement has been confirmed by SaskPower Boundary Dam Carbon Capture Project (located in Saskatchewan, Canada), which is the world largest and the first commercial amine based CO\textsubscript{2} capture plant with 1.0 million tons of capturing CO\textsubscript{2} annually. Within the first few years of its operation, more than 2.0 million tons of CO\textsubscript{2} has been captured from the coal fired Boundary Dam power generation plant [2].

In the amine based CO\textsubscript{2} absorption, CO\textsubscript{2} is captured from feed gas by counter currently flowed reactive chemical solvent. The CO\textsubscript{2}-rich solvent leaves from the bottom of absorber and is pumped to the stripper to discharge CO\textsubscript{2}. The CO\textsubscript{2}-lean solvent is then recycled to the absorber [3]. Typical amines used in the absorption are monoethanolamine (MEA), N-methylpyrrolidone (MDEA), 2-amino-2-methyl-1-propanol (AMP), and piperazine (PZ) [4]. Since each amine has its advantages and disadvantages, it has therefore been reported in the literature that one of the successive keys for this technology is to use a highly effective solvent. As a result, numbers of novel amines have been developed, synthesized, and screened [3].

At present, N-methyl-4-piperidinol (MPDL), a cyclical tertiary amine, shows great potential to use as an alternative solvent in substitution of the conventional amine. This is because MPDL possesses very high absorption capacity, reasonable absorption rate, and considerably low energy requirement for solvent regeneration [5], [6]. However, one of its major drawbacks is that MPDL has too slow CO\textsubscript{2} absorption rate comparing with industrial benchmarking MEA [6]. Therefore, MPDL is not suitable to use as a single solvent. Based on its very high absorption capacity and considerably low energy requirement for solvent regeneration [5], MPDL should be blended with highly reactive amine. It is expected that the blending two amines will enrich the advantages of each amine and encounter the disadvantages of one amine by another amine [4].

As a stericly hindered primary amine, AMP is one of the most commonly used solvents because of its high reactivity with CO\textsubscript{2} [3]. Additionally, due to the sterically hindered effect, instable AMP-carbamate is formed after CO\textsubscript{2} absorption. The AMP-carbamate is easily hydrolyzed to bicarbonate and free AMP. The free amine can then react with CO\textsubscript{2} again. Thus, the absorption capacity of AMP is reported to be higher than MEA. Therefore, three novel formulated solvent of MPDL-AMP should be further investigate for its potential to use as alternative promising solvents in substation of industrial benchmarking MEA. The chemical structures of the four amines are presented in Table I.

Table I.

Manuscript received December 29, 2019; revised August 2, 2020. This work was supported by Grants for Development of New Faculty Staff, Ratchadaphiseksomphot Endowment Fund, Chulalongkorn University, Thailand. The authors would also like to acknowledge the support from The Thailand Research Fund and Office of the Higher Education Commission (Research Grant for New Scholar: MRG6200187), and Mahidol University, Thailand.

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doi: 10.18178/ijesd.2020.11.10.1294
TABLE I: CHEMICAL STRUCTURE OF AMINES (MPDL AND AMP) USED IN THE PRESENT WORK

| Amine | Molecular weight (g/mol) | Chemical structure | Amine classification | CAS No. |
|-------|-------------------------|--------------------|---------------------|---------|
| MPDL  | 115.17                  | ![MPDL structure](image) | Cyclic tertiary amine | 106-52-5 |
| AMP   | 89.14                   | ![AMP structure](image) | Sterically hindered primary amine | 124-68-5 |

It is important to mention that in order to effectively design the hydrodynamics parameters (e.g., gas flow rate, liquid flow rate, and liquid to gas flow ratio) in the absorption column, the physical properties of the amine solvents (including density and viscosity) are required. Additionally, a determination of the reaction kinetics and mass transfer parameters (e.g., overall reaction rate constant, second-order reaction rate constant, enhancement factor, and mass transfer coefficient), density, viscosity and physical CO₂ diffusivity of the amine solvents are needed. Those reaction kinetics and mass transfer parameters are essential for designing the absorption column. Since the formulated MPDL-AMP solvent used in the present work is newly developed, the experimental data on its density, viscosity, and physical CO₂ diffusivity have therefore not yet been measured. Thus, the data reported in this work will be very useful for further studying on hydrodynamics of the solvents, kinetics and mass transfer of the CO₂ absorption, and designing the absorption column.

As discussed above, highly reactive amine (in this case, AMP) should be blended with MPDL to improve its CO₂ absorption kinetics or reactivity. Since 30% wt. total amine concentration is widely accepted to be generally used in the industry, the blended ratios of MPDL and AMP were then varied at 25/5%wt., 20/10%wt., and 15/15%wt., respectively. In the present work, the density and the viscosity were measured over a temperature range of 303-333 K, which is an actual absorber temperature in the industry.

II. EXPERIMENTAL SECTION

A. Chemicals

MPDL with a purity of 98% and AMP with a purity of 95% were obtained from Sigma-Aldrich, Switzerland. CO₂ with a purity of 99% were supplied by Linde (Thailand) PCL. All materials in this study were used as received without further purification.

B. Density

The density of MPDL based solvents were measured by a 25 mL adjusted Gay-Lussac pycnometer (WINTEG Co., Germany). The operating temperatures of 303-333 K were controlled by a temperature controlled water bath (ISOTEMP2150, Fisher Scientific Inc., USA) with an operating range of 293-373 K and a temperature stability of ±0.02°C. The pycnometer and the procedure of measuring solvent density were validated with pure MEA and 5.0 M MEA over temperature of 303-333 K as described in our previous work [6]. The results showed that the absolute average deviation percentages (%AADs) were 0.70% and 0.48%, respectively. Thus, it infers that the equipment and procedure used in the present work are accurate and can be used to determine the density of novel formulated MPDL-AMP solvent.

C. Viscosity

The kinematic viscosity of novel formulated MPDL-AMP solvent was measured by a capillary Cannon-Fenske Routine Viscometer (Cannon Instrument Co., USA). The variation of solvent’s temperature was also controlled by a temperature controlled water bath (ISOTEMP2150, Fisher Scientific Inc., USA) with an operating range of 293-373 K and a temperature stability of ±0.02°C. An experimental procedure was reported in our previous work [6]. It should be noted that the dynamic viscosity of the solvent can be calculated based on its density and kinematic viscosity. Additionally, the results showed that the dynamic viscosity of pure MEA and 5.0 M MEA well corresponded with the reference values [7]-[9] with AADs of 1.49% and 1.42%, respectively. Thus, it can be said that the equipment and procedure for measuring the dynamic viscosity was accurate and reliable.

D. Physical Diffusivity of CO₂

It is generally known that CO₂ reacts chemically with amine, thus the physical diffusivity of CO₂ cannot be measured directly. Typically, the physical diffusivity of CO₂ in aqueous amine solvent can be determined by N₂O analogy by measuring its physical N₂O diffusivity [4], [10]. The experiment can be done in laminar jet absorber [11]. However, the experiment is time-consuming and costly. In the present work, the physical diffusivity of CO₂ in novel formulated MPDL-AMP solvent were then calculated through its dynamic viscosity by modified Stokes-Einstein equation [10].

III. RESULTS AND DISCUSSION

A. Density of MPDL-AMP Solvent

The density of aqueous solutions of novel formulated MPDL-AMP was experimentally measured over a temperatures and MPDL/AMP blended ratios of 303-333 K and 25/5%wt.-15/15%wt., respectively. The results are presented in Table II and plotted in Fig. 1.

It can be seen from Table II and Fig. 1 that the density of aqueous solutions of MPDL-AMP decreased as temperature increased. This observation is in good agreement with the density of water, 30%wt. MEA, and 30% wt. AMP presented in the literature [8], [9]. Additionally, it can be found that the density of aqueous solutions of MPDL-AMP decreased as concentration of AMP decreased. This is because the density of pure AMP is lower than that of pure MPDL [6]. It should also be mentioned that the density of aqueous solutions of MPDL-AMP was found to be slightly lower than that of 30%wt. MEA and slightly higher than that of 30% wt. AMP. Based on this observation, it can be said that the novel formulated solvent of MPDL-AMP over a concentration range of 25/5%wt. to 15/15%wt. can be used for capturing CO₂ based on its density.
The effect of temperature on the MPDL solvent was experimentally measured at various concentrations and temperatures. From the density data, the dynamics viscosity can be determined and presented in Table IV and Fig. 2. It can be observed that the viscosity of aqueous solutions of novel formulated MPDL-AMP solvent decreased as temperature increased over a temperature range of 313-333 K. The effect of temperature on the MPDL-AMP viscosity obtained in the present work is in good agreement with the literature data as shown in (6). Additionally, it can be found that the viscosity of aqueous solutions of novel formulated MPDL-AMP solvent increased as concentration of AMP in the blended solvent increased. This is due to the fact that the viscosity of pure AMP is higher than that of pure MPDL [6].

In order to predict the dynamics viscosity of the novel formulated MPDL-AMP solvent over range of concentration and temperature used in the present work, the predictive correlation based on polynomial model was developed. According to the results presented in Table IV and Fig. 2, it can be seen that the viscosity is a function of both amine concentration and temperature. Thus, in this work, the predictive correlation was then expressed as a function of both amine concentration and temperature as shown in (5).

\[ \mu = B_0 + B_1C + B_2C^2 \]  (5)

where \( C \) is concentration of MPDL in the blended solvent (%wt.), and \( B_0, B_1, \) and \( B_2 \) are temperature dependent coefficients, which are a function of temperature (T) in Kelvin as shown in (6)-(8).

\[ B_0 = d + eT + fT^2 \]  (6)

\[ B_1 = d' + e'T + f'T^2 \]  (7)
\[ B_2 = d^2 + e^2 T + f^2 T^2 \]  \hspace{1cm} (8)

By applying non-linear regression analysis, the constant parameters for the temperature dependent coefficients \( (B_0, B_1, \text{ and } B_2) \) can be obtained and presented in Table V. The predicted results are showed in Fig. 2 as solid lines. It can be seen that the predicted results very well correspond with the experimental data with AAD of 1.23%.

![Fig. 2. Dynamics viscosity of aqueous solutions of MPDL-AMP at various concentrations and temperature; dots are the experimental data, solid lines are predicted data from the correlation developed in this work, and dash lines are literature data of MEA, MDEA, and AMP [8].](image)

### TABLE V: CONSTANT PARAMETERS FOR THE TEMPERATURE DEPENDENT COEFFICIENT USED IN VISCOSITY ESTIMATION

| Temperature dependent coefficient | Constant parameter |
|-----------------------------------|--------------------|
| \( B_0 \)                          | \( d \) 115.0143   |
|                                   | \( e \) -0.65879    |
|                                   | \( f \) 0.000952    |
| \( B_1 \)                          | \( d' \) 140.6003   |
|                                   | \( e' \) -0.71528   |
|                                   | \( f' \) 0.00091    |
| \( B_1 \)                          | \( d'' \) -506.211  |
|                                   | \( e'' \) 2.49554   |
|                                   | \( f'' \) -0.00302  |

### C. Physical CO₂ Diffusivity in MPDL-AMP Solvent

In this work, the physical diffusivity of CO₂ in aqueous solutions of novel formulated MPDL-AMP were calculated from its dynamics viscosity through the modified Stokes-Einstein equation as can be written as (9).

\[ D_{CO_2-MPDL-AMP} \mu_{MPDL-AMP}^{0.8} = D_{CO_2-water} \mu_{water}^{0.8} \]  \hspace{1cm} (9)

where \( D_{CO_2-MPDL-AMP} \) is physical diffusivity of CO₂ in aqueous MPDL-AMP solutions (m²/s), \( D_{CO_2-water} \) is physical diffusivity of CO₂ in water (m²/s), \( \mu_{MPDL-AMP} \) is dynamics viscosity of aqueous MPDL-AMP solutions (mPa.s), and \( \mu_{water} \) is dynamics viscosity of water (mPa.s).

As presented in Fig. 3, the physical diffusivity of CO₂ in aqueous solutions of MPDL-AMP solvent decreased as concentration of AMP in the blended solvent increased. This is because as the concentration of AMP in the blended solvent increased, the solvent viscosity increased as shown in Table IV and Fig. 2. It is more difficult for CO₂ to physically diffuse through the higher viscosity solvent, thus the physical diffusivity of CO₂ was then found to be decreased. Additionally, it can be seen that the physical diffusivity of CO₂ in aqueous solutions of MPDL-AMP is much lower than that of water because the viscosity of MPDL-AMP solvent is much higher than that of water. For the effect of temperature, it can be seen from Fig. 3 that the physical diffusivity of CO₂ increased as temperature increased. It can be reasoned that at elevated temperature, the viscosity of solvent decreases and there is higher driving force for CO₂ diffusing through the solvent.

![Fig. 3. Physical diffusivity of CO₂ in aqueous solutions of MPDL-AMP obtained from the present work and that of water obtained from the literature [10].](image)

### IV. CONCLUSION

In the present work, density, viscosity, and physical CO₂ diffusivity of novel formulated MPDL-AMP solvents were investigated. The density and the viscosity were experimentally measured over ranges of concentrations and temperatures of 25%wt. MPDL/5%wt. AMP to 15%wt. MPDL/15%wt. AMP and 313 K to 333 K, respectively. The physical diffusivity of CO₂ in novel formulated MPDL-AMP solvent was calculated based on its measured viscosity using the modified Stokes-Einstein Equation. It was found that both amine concentration and temperature affected density, viscosity, and physical CO₂ diffusivity of the MPDL-AMP solvent. Additionally, it should be mentioned that the density and the viscosity of novel formulated MPDL-AMP solvent were found to be in the same ranges of conventional amines used in CO₂ capture process. Therefore, based on its density and viscosity, the novel formulated MPDL-AMP solvent can be considered as a potential alternative solvent to be further investigated for CO₂ capture applications.

### CONFLICT OF INTEREST

The authors declare no conflict of interest.

### AUTHOR CONTRIBUTIONS

TS is the corresponding author for this work, he initiated the original concept of this work by blending MPDL with AMP and designed all experimental procedures, planning, and experimental conditions. TS also analyzed the data and wrote the paper. TK and PN conducted the experiment during their Bachelor’s degree under the supervision of TS. PP and RJ reviewed the manuscript. All authors had approved the final version.
ACKNOWLEDGMENT
This work was supported by Grants for Development of New Faculty Staff, Ratchadaphiseksomphot Endowment Fund, Chulalongkorn University, Thailand. The authors would also like to acknowledge the support from The Thailand Research Fund and Office of the Higher Education Commission (Research Grant for New Scholar: MRG6280187), and Mahidol University, Thailand.

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