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Amine-based Carbon Dioxide Absorption: The Ionic Strength Effect on the Monoethanolamine Protonation Constant at Temperatures from 313 to 333K

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Amine-based absorption has been extensively used for carbon dioxide (CO_2) removal processes, such as CO_2 absorption from flue gas as well as from natural gas. As a reactive system in which the chemical reaction, as well as mass transfer, occur simultaneously, an experimental determination of equilibrium reaction constants, e.g. acid dissociation/protonation constant (K_a), is, therefore, necessary to be conducted. This study aims to evaluate the ionic strength effect from 0.06 to 6.0 m (mol/kg water) on the K_a value of monoethanolamine (MEA) at temperatures between 313 and 333K. The experimental results indicate that the pK_a values tend to be increasing as the ionic strength increases. This is contradicting to the temperature effect where the pK_a values tend to be decreasing as the temperature increases. Furthermore, the extended Debye-Hückel formulation was implemented to predict the species activity coefficients.

Keywords: Absorption, activity coefficient, carbon dioxide, monoethanolamine, protonation constant

INTRODUCTION

In addition to methane (CH_4), the global warming problem is also caused by carbon dioxide (CO_2) emission which may come from carbon-based fuel combustion, gas sweetening processes, iron and steel industry, etc. It is, according to Ma'mun et al. (2018a, 2018b), stated that the emission of CO_2 increases every year. Some countries, therefore, attempt to reduce their CO_2 emissions by the implementation of Carbon Capture and Storage (CCS) technology, for instance.

A commercial CO_2 absorbent must fulfil some criteria such as high reaction rate as well as high net cyclic capacity (Ma'mun et al., 2007a). Moreover, the other commercial CO_2 absorbent criteria were reported elsewhere (Li et al., 1994; Jou et al., 1995; Liu et al., 1999; Hoff et al., 2013). Thus, research on CO_2 capturing solvent development to discover promising systems has been conducted, such as amines (Idem et al., 2006; Ma'mun et al., 2007b), carbonate (Lu et al., 2011),

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amino acid salts (Knuutila et al., 2011; Ma'mun and Kim, 2013), chilled ammonia (Alstom, 2007), etc.

To develop a promising system and also to improve thermodynamic and kinetic models, an acid dissociation/protonation constant (K_a) is an important factor where a high pK_a value is required for a promising CO_2 absorbent. According to Hartono et al. (2014), a solvent with high pK_a offers fast kinetic in binding CO_2, thus it will reduce the absorber dimension.

In comparison to secondary and tertiary amines, the aqueous solutions of MEA ($H_2NCH_2CH_2OH$), a primary amine, were widely used for many years for the CO_2 and H_2S removal (Kohl and Nielsen, 1997). In addition, even though some efficient systems have been implemented especially for the high-pressure natural gas treatment, some researchers have been conducting intensive research on MEA up to now to improve its performances (Idem et al., 2006; Sønderby et al., 2013; Iliuta and Larachi, 2018; Wang et al, 2019). This means that research on MEA is still of importance hitherto.

In this study, the pK_a of an aqueous solution of MEA was evaluated at different ionic strengths (0.06 to 6.0 m) and different temperatures from 313 to 333K. Previously, pK_a values of MEA at different ionic strengths were evaluated by Ma'mun et al. (2019) at 303K. The experiments were conducted at typical temperatures for the actual CO_2 absorption (i.e. 303 to 333K) in the CO_2 capture plants by the use of aqueous MEA solutions in both tray and packed bed columns (Kohl and Nielsen, 1997).

MATERIALS AND METHOD

Materials

Some chemicals obtained from Sigma-Aldrich were used to determine pK_a values such as min. 98 mass % MEA and min. 99.8 mass % sodium chloride (NaCl). Moreover, 37 mass % hydrochloric acid (HCl) from Merck was used as the titrant. The pH meter was calibrated by standardized pH solutions (pH 4.00 and 7.00).

Apparatus and Method

In this experiment, it was used similar apparatus as that used by Ma'mun et al. (2017a, 2017b, 2019). The apparatus was submerged in a water bath consisting of a 300-mL jacketed glass reactor equipped by a pH meter, a thermometer, and a stir bar. A circulating pump was used to circulate a heating medium through the reactor. An analytical balance and a 5-mL syringe were also used in this study. A detailed procedure can be found elsewhere (Ma'mun et al., 2019).

ACTIVITY COEFFICIENT MODEL

In aqueous solution, a protonated amine (AmH^+) will be decomposed into a free amine (Am) and a proton (H^+) as written in Eq. (1) with an equilibrium/ protonation constant defined in Eq. (2).

$$\mathrm{AmH^+} \leftrightarrow \mathrm{Am} + \mathrm{H^+} \tag{1}$$

$$K_\mathrm{a} = \frac{a_\mathrm{Am} \; a_\mathrm{H^+}}{a_\mathrm{AmH^+}} \tag{2}$$

Rearranging Eq. (2) yields a correlation between pK_a and pH as follows:

$$pK_a = pH - log\left[\frac{\gamma_{\mathrm{Am}} C_{\mathrm{Am}}}{\gamma_{\mathrm{AmH^+}} C_{\mathrm{AmH^+}}}\right] \quad (3)$$

If the solution is an ideal one where free amine and protonated amine activity coefficients ($\gamma_{\mathrm{Am}}, \gamma_{\mathrm{AmH^+}}$) are unity, Eq. (3) can then be written as:

$$pK_a = pH - log\left[\frac{C_{\mathrm{Am}}}{C_{\mathrm{AmH^+}}}\right] \quad (4)$$

In this work, the species activity coefficients were determined by the use of the extended Debye-Hückel equation (Debye and Hückel, 1923) as written in Eq. (5).

$$ln\gamma_{\mathrm{i}} = \frac{-2.303 A_\gamma z_{\mathrm{i}}^2 I^{1/2}}{1 + B a_{\mathrm{i}} I^{1/2}} + 2\sum_{\mathrm{j}} \beta_{\mathrm{ij}} m_{\mathrm{j}} \quad (5)$$

The first term of Eq. (5) is the electrostatic forces while the latter is the short-range van der Waals forces in which its contribution is insignificant, this second term can, therefore, be disregarded. A_γ and B are the temperature and the solvent dielectric constant dependent; their values can then be found elsewhere (Kielland, 1937; Manov et al., 1943). The solution ionic strength I is a function of the molality m_{j} and the charge number on the ion z_{j} as written in Eq. (6).

$$I = \frac{1}{2}\sum_{\mathrm{j}} m_{\mathrm{j}} z_{\mathrm{j}}^2 \quad (6)$$

Due to a lack of information, for all ions, a_{i} is usually set to 4 Å in which this effective diameter of the ion i would be different for different ions and would possibly also be a function of both the ionic strength and the composition of solvent (Ma'mun et al., 2006).

Furthermore, the protonated amine and free amine concentrations ($C_{\mathrm{AmH^+}}, C_{\mathrm{Am}}$) can be determined by rearranging Eq. (3) and the amine mass balance as the following:

$$C_{\mathrm{AmH^+}} = \frac{C_{\mathrm{Am}}^{\mathrm{o}}}{\left(\frac{\gamma_{\mathrm{AmH^+}}}{\gamma_{\mathrm{Am}}}\right) 10^{(pH - pK_a)} + 1} \quad (6)$$

$$C_{\mathrm{Am}} = C_{\mathrm{Am}}^{\mathrm{o}} - C_{\mathrm{AmH^+}} \quad (7)$$

The pK$_a$ value was determined at which the accumulated titrant volume is half of the total volume to reach the Equivalence Point (EP); at this point, pK$_a$ equals pH (Ma'mun et al., 2017b).

RESULTS AND DISCUSSION

MEA protonation constants were determined at temperatures from 313 to 333K for different ionic strengths *I* (0.06 – 6.0 m) using the potentiometric titration (PT) method and an aqueous solution of 0.1 M HCl was used as the titrant. The detailed explanation of the method can be seen in Ma'mun et al. (2019). The ionic strength effect was made by adding some NaCl into the aqueous MEA solutions with the amounts from 0.01 to 6.0 m. In fact, the ionic strength of the solutions will slightly increase due to the presence of other ions, such as protonated MEA (MEAH$^+$), H$^+$, OH$^-$, and Cl$^-$ ions from the ionization of the titrant HCl.

The addition of NaCl was up to 6.0 m. This is to make a comparable ionic strength effect when the aqueous solutions of MEA are employed as the CO_2 absorbent with the concentrations up to 30wt% (approx. 7.0 m). Since the absorption process, in general, takes place at basic (alkaline) condition, a 30wt%

aqueous solution of MEA at pH 8 may give the ionic strength from the protonated MEA for about 3 m and the contribution of other ions may slightly increase the solution ionic strength. That is why the addition of 6.0 m in this study may cover the upper limit of the ionic strength for the aqueous solution of 30wt% MEA.

Fig. 1 shows the pK_a measurement results in which the higher the ionic strengths the higher the pK_a values at a constant temperature. Moreover, the pK_a values decrease as the temperature increase at a constant ionic strength. This phenomenon, according to Hartono et al. (2014), is due to the effect of salting out at high solution ionic strength, causing higher pK_a and pH values at the beginning. Thus the solution ionic strength effect cannot be neglected.

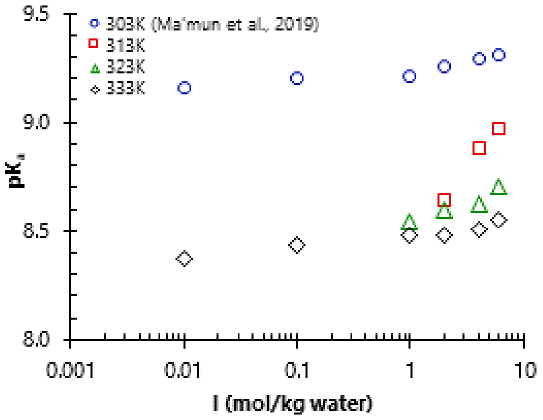

Fig. 1: Relationship between pK_a of MEA vs. the ionic strength at different temperatures

The pK_a can also be represented in the form of K_a as a function of the ionic strength. As seen in Fig. 2, that the relationship between ln K_a and the ionic strength gives linear expressions, with the equation as follows:

$$lnK_a = \frac{C_1 I^{1/2}}{1 + I^{1/2}} + C_2 \qquad (8)$$

where C_1 and C_2 equal −0.516 and −21.03 for 303K, −6.182 and −16.29 for 313K, −1.507 and −18.91 for 323K, −0.544 and −19.25 for 333K, respectively.

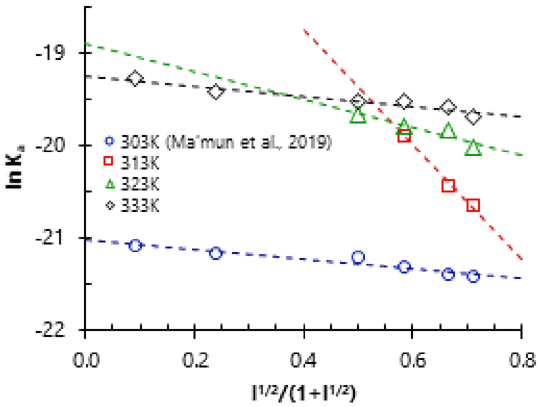

Fig. 2: Regression values of K_a as a function of ionic strengths

According to Eq. (3), when pH equals pK_a, both free MEA activity (a_{MEA}) and protonated MEA activity ($a_{\mathrm{MEAH^+}}$) are, therefore, the same. This is confirmed by the experimental results in which as seen in Fig. 3, at the total ionic strength of 0.06 m, $a_{\mathrm{MEAH^+}}$ decreases as pH increases, while a_{MEA} increases as pH increases. These values intersect at pH 8.37 which is similar to the experimental pK_a value at 333K. In addition, if the concentrations of the free MEA and MEAH$^+$ ($C_{\mathrm{MEA}}, C_{\mathrm{MEAH^+}}$) are plotted, they will intersect at pH 8.46 which is slightly higher than the pK_a value from the experiment. This means that the activity coefficient of MEAH$^+$ ($\gamma_{\mathrm{MEAH^+}}$) is not equal to unity, i.e. non ideal system. In this figure, the activity and the concentrations of MEA and MEAH$^+$ at the total ionic strength of 4.05 m are also presented and show a similar trend.

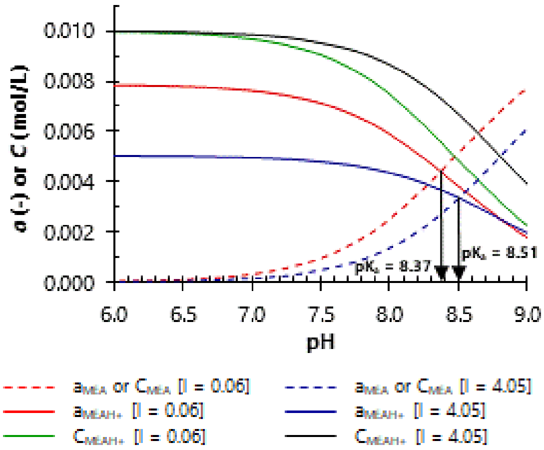

Fig. 3: The activity and concentration of species as a function of pH at the ionic strengths of 0.06 and 4.05 m at 333K

Based on Eq. (5) by disregarding the short-range VdW forces, the activity coefficient of free MEA (γ_{MEA}) is unity for all the ionic strength values, this is because MEA is a neutral species. While $\gamma_{\mathrm{MEAH^+}}$ is about 0.787 at the total ionic strength of 0.06 m at 333K. The total ionic strength is contributed by several ions existing in the solution, such as Na^+, Cl^-, $MEAH^+$, H^+, and OH^- in which more than 72% of the total ionic strength comes from the contribution of ion Cl^- from the ionization of HCl. Moreover, at the total ionic strength of 4.05 m (mostly from the salt background NaCl), $\gamma_{\mathrm{MEAH^+}}$ is found to be about 0.505. However, the activity coefficients of $MEAH^+$ and the ionic strengths change during titration as pH changes. The changes in them can be seen in Fig. 4. The activity coefficients of $MEAH^+$ are relatively constant from pH 4 to 7, but they decrease at pH < 4. This occurs because the ionic strengths start to sharply increase as the concentration of ions increases due to dilution of the titrant, i.e. HCl. This has also been confirmed by Hartono et al. (2014) in which the solution ionic strength from the titrant dilution should be taken into account. In Fig 4b, the ionic strengths seem to be slightly constant during titration. Since the ionic strength from the salt background was already high, i.e. 4.0 m, the ionic strength contribution from the titrant dilution can then be disregarded.

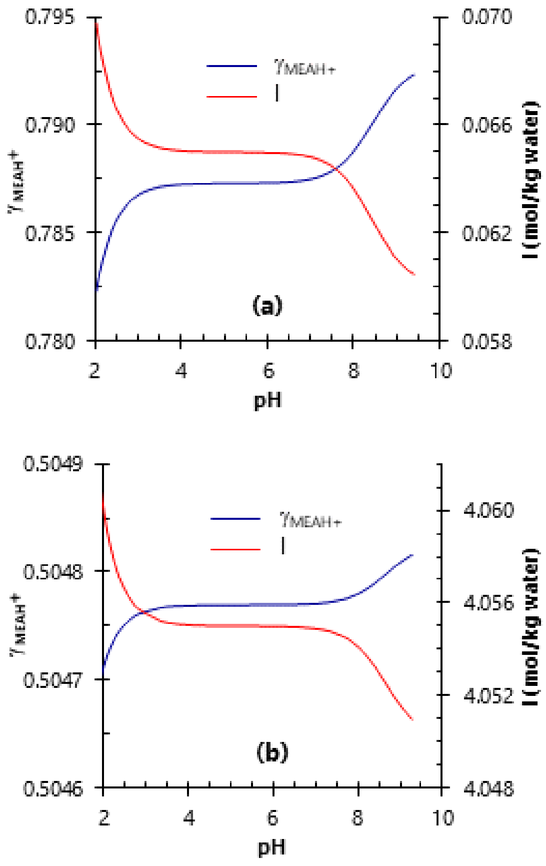

Fig. 4: Change in $\gamma_{\mathrm{MEAH^+}}$ as a function of pH at 333K, (a) Low ionic strengths (0.06 – 0.07 m), (b) High ionic strengths (4.05 – 4.06 m)

CONCLUSIONS

The ionic strength effect on the MEA protonation constant was evaluated at different ionic strengths (0.06 to 6.0 m) at 313 to 333K by the PT method. It can be concluded that, in general, the pK_a will increase as the ionic strengths increase. In addition, the extended Debye-Hückel equation was used to determine the species activity coefficient. It can be observed that as the pH decreases the free MEA activity decreases, but the activity of the protonated MEA increases at a certain ionic strength.

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NOMENCLATURE

a : activity [–]
a_i : ion i effective diameter [Å]
Am : amine
AmH^+ : protonated amine
A_γ : the Debye-Hückel limiting slope
C : concentration [mol/L]
K_a : protonation constant
I : ionic strength [mol/kg water]
m : molality [mol/kg water]
z : ion charge number
γ : activity coefficient [–]

REFERENCES

1. Alstom. (2007). "Chilled ammonia-based wet scrubbing for post-combustion CO_2 capture", DOE/NETL report No. 401/021507
2. Debye, P., Hückel, E. (1923). "The theory of electrolyte", *Physikalische Zeitschrift,* 24, 185–206
3. Hartono, A., Saeed, M., Kim, I., Svendsen, H. F. (2014). "Protonation constant (pK_a) of MDEA in water as function of temperature and ionic strength", *Energy Procedia*, 63, 1122–1228
4. Hoff, K. A., da Silva, E. F., Kim, I., Grimstvedt, A., Ma'mun, S. (2013). "Solvent development in post combustion CO_2 capture – Selection criteria and optimization of solvent performance, cost and environmental impact", *Energy Procedia*, 37, 292–299
5. Idem, R., Wilson, M., Tontiwachwu-thikul, P., Chakma, A., Veawab, A., Aroonwilas, A., Gelowitz, D. (2006). "Pilot plant studies of the CO_2 capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO_2 capture technology development plant and the Boundary Dam CO_2 Capture Demonstration Plant", *Ind. Eng. Chem. Res.*, 45, 2414–2420
6. Iliuta, I., Larachi, F. (2018). "CO2 and H2S absorption by MEA solution in packed-bed columns under inclined and heaving motion conditions - Hydrodynamics and reactions performance for marine applications", *Int. J. Greenh. Gas Con.*, 79, 1–13
7. Jou, F. Y., Mather, A. E., Otto, F. D. (1995). "The solubility of CO_2 in a 30 mass percent monoethanolamine solution", *Can. J. Chem. Eng.*, 73, 140–147
8. Kielland, J. (1937). "Individual activity coefficients of ions in aqueous

solutions", *J. Am. Chem. Soc.* 59, 1675–1678

9. Knuutila, H., Aronu, U. E., Kvamsdal, H. M., Chikukwa, A. (2011). "Post combustion CO_2 capture with an amino acid salt", *Energy Procedia*, 4, 1550–1557
10. Kohl, A. L., Nielsen, R. B. (1997). Gas Purification 5th ed., Gulf Publishing Company, Houston, Texas, U. S. A.
11. Li, Y. G., Mather, A. E. (1994). "Correlation and prediction of the solubility of carbon dioxide in a mixed alkanolamine solution", *Ind. Eng. Chem. Res.*, 33, 2006–2015
12. Liu, Y., Zhang, L., Watanasiri, S. (1999). "Representing vapor-liquid equilibrium for an aqueous MEA-CO_2 system using the Electrolyte Nonrandom–Two–Liquid Model", *Ind. Eng. Chem. Res.*, 38, 2080–2090
13. Lu, Y., Ye, X., Zhang, A., Khodayari, A., Djukadi, T. (2011). "Development of a carbonate absorption-based process for post-combustion CO_2 capture: the role of biocatalyst to promote CO_2 absorption rate", *Energy Procedia*, 4 1286–1293
14. Ma'mun, S., Amelia, E., Rahmat, V., Alwani, D. R., Kurniawan, D. (2017a). "Design of protonation constant measurement apparatus for carbon dioxide capturing solvents", *IOP Conf. Ser., Mater. Sci. Eng.*, 162, 012003
15. Ma'mun, S., Chafidz, A., Indrayanto, E., Setiawan, P. K. (2019). "The effect of ionic strength on protonation constant of monoethanolamine in water at 303K", *J. Phys.: Conf. Ser.*, 1295, 012017
16. Ma'mun, S., Dindore, V. Y., Svendsen, H. F. (2007a). "Kinetics of the reaction of carbon dioxide with aqueous solutions of 2-((2-aminoethyl)amino) ethanol", *Ind. Eng. Chem. Res.*, 46 385–394
17. Ma'mun, S., Jakobsen, J. P., Svendsen, H. F., Juliussen, O. (2006). "Experimental and modeling study of the solubility of carbon dioxide in aqueous 30 mass % 2-((2-aminoethyl)amino)ethanol solution", *Ind. Eng. Chem. Res.*, 45, 2505–2512
18. Ma'mun, S., Kamariah, Sukirman, Kurniawan, D., Amelia, E., Rahmat, V., Alwani, D. R. (2017b). "Experimental determination of monoethanolamine protonation constant and its temperature dependency", *MATEC Web of Conf.*, 101, 02001
19. Ma'mun, S., Kim, I. (2013). "Selection and characterization of phase-change solvent for carbon dioxide capture: precipitating system", *Energy Procedia*, 37, 331–339
20. Ma'mun, S., Sukirman, Alel, A. E., Hasanah, M. (2018a). "Building electricity consumption as an indicator of indirect carbon dioxide emissions", *IOP Conf. Ser., Mater. Sci. Eng.*, 358, 012012
21. Ma'mun, S., Svendsen, H. F., Bendiyasa, I M. (2018b). "Amine-based carbon dioxide absorption: evaluation of kinetic and mass transfer parameters", *J. Mech. Eng. Sci.*, 12, 4088–4097
22. Ma'mun, S., Svendsen, H. F., Hoff, K. A., Juliussen, O. (2007b). "Selection of new absorbents for carbon dioxide

capture", *Energ. Convers. Manage.*, 48, 251–258

23. Manov, G. G., Bates, R. G., Hamer, W. J., Acree, S. F. (1943). "Values of the constants in the Debye–Hückel equation for activity coefficients", *J. Am. Chem. Soc.*, 65, 1765–1767
24. Sønderby, T. L., Carlsen, K. B., Fosbøl, P. L., Kiørboe, L. G., von Solms, N. (2013). "A new pilot absorber for CO2 capture from flue gases: Measuring and modelling capture with MEA solution", *Int. J. Greenh. Gas Con.*, 12, 181–192
25. Wang, J., Deng, S., Sun, T., Xu, Y., Li, K., Zhao, J. (2019). "Thermodynamic and cycle model for MEA-based chemical CO_2 absorption", *Energy Procedia*, 158, 4941–4946