The Effect of Ionic Strength on Protonation Constant of Monoethanolamine in Water at 303K

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Abstract. Amine-based absorption is a reactive system in which mass transfer and chemical reaction take place simultaneously. Protonation constant (pKa) is an important equilibrium reaction parameter that can be determined experimentally. The objective of this study is to evaluate the pKa of monoethanolamine (MEA) at different ionic strengths ranging from 0.01 to 6 moles of NaCl/kg of water at 303K by a potentiometric titration method. The results show that the pKa values, in general, increase as the ionic strengths increase. Moreover, the activity coefficients of species were also determined by the extended Debye-Hückel model. The pKa data and the activity coefficients obtained from this work could then be used for the kinetic and thermodynamic modeling in the absorber and desorber design.

1. Introduction
In addition to methane (CH4), carbon dioxide (CO2) emission from combustion and acid gas separation processes causes the global warming problem. It is reported that the CO2 emission increases annually [1]. Therefore, attempts on reducing CO2 emission have been conducted by some parties using e.g. Carbon Capture and Storage (CCS) technology.

Carbon dioxide absorbent with a high reaction rate and high net cyclic capacity is a must [2]. In addition, other criteria that need to be considered were reported elsewhere [3–7]. Thus, some researchers conduct intensive research on development of CO2 capturing solvents to find promising solvent candidates, such as amines, amino acid salts (AAS), sodium carbonate, etc. [8–13].

To develop new solvent systems as well as to get better kinetic and thermodynamic model, the protonation constant (pK_a) is such an important parameter in which a high pK_a value is required for a promising candidate solvent that will be implemented in post combustion capture (PCC) process. It has been proved that a solvent with high pK_a results in fast kinetic to bind CO2 which in turn reducing absorption column dimension [14].

The study aims to evaluate pK_a of MEA (H2NCH2CH2OH), a primary amine with a molecular structure given in Figure 1, in water at different ionic strengths at 303K by use of a potentiometric titration (PT) method.

Figure 1. Molecular structure of MEA
2. Materials and Method

2.1. Materials
MEA (min. 98 mass %) and sodium chloride (NaCl) p.a. (min. 99.8 mass %) were used in this work and were obtained from Sigma-Aldrich. In addition, sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) from Merck with purity of min. 96.0 mass % was used as titrant and buffer solutions (pH 4.00 and 7.00) were used to calibrate pH probe.

2.2. Apparatus and Procedure
The apparatus used in this study was similar to that used by [15] as shown in Figure 2, consisting of a jacketed glass (300 mL, equipped by a thermometer, a pH meter, and a stir bar), a waterbath with a circulating pump, a balance, and a syringe (5 mL).

The experiments were conducted in a glass reactor previously filled by approximately 50 g of aqueous solution of 0.01 mol MEA/kg water at 303K. NaCl was added to make a certain ionic strength (I) of the solution (max 6 mol NaCl/kg water). The solution was then titrated by 0.1 M H\textsubscript{2}SO\textsubscript{4} solution. It was required ~5 g of titrant per run. Similar titration procedure can be found elsewhere [15].

![Figure 2. pK\textsubscript{a} measurement apparatus: (1) jacketed glass, (2, 3) magnetic stirrer and stir bar, (4) pH meter, (5) thermometer, (6, 7) medium inlet-outlet, (8) waterbath, (9) circulating pump, (10) balance, and (11) syringe](image-url)

2.3. Protonation Constant Determination and Activity Coefficient Model
According to [15], reaction of amine protonation is:

\[
\text{AmH}^+ \leftrightarrow \text{Am} + \text{H}^+
\]  

(1)

The equilibrium/protonation constant of the reaction (1) is defined as:

\[
K_a = \frac{a_{\text{Am}} \cdot a_{\text{H}^+}}{a_{\text{AmH}^+}}
\]

(2)

where \(a\), \(\text{Am}\), and \(\text{AmH}^+\) refer to the activity of the species, amine, and protonated amine, respectively. Equation (2) can also be written in the form of:

\[
pK_a = pK + \log \left( \frac{\gamma_{Am} m_{Am}}{\gamma_{AmH} m_{AmH}} \right)
\]

(3)
The extended Debye-Hückel (DH) equation [16] is used to determine the species activity coefficients as written in Equation (4).

\[ \ln \gamma_i = \frac{-2.303 A_i z_i^2 I^{1/2}}{1 + B a I^{1/2}} + 2 \sum_j \beta_j m_j \]  

(4)

The first and second terms of Equation (4) represent the electrostatic and the Van der Waals (VdW) forces, respectively. However, the VdW forces contribution is insignificant, therefore, this term is then disregarded. \( A_i, a_i, \) and \( B \) are the DH limiting slope, the ion \( i \) effective diameter, and a parameter depending on temperature and the solvent dielectric constant, respectively. The values of \( A_i, a_i, \) and \( B \) can be found elsewhere [17, 18]. As seen in the equation, \( I \) is the ionic strength and is defined as follows:

\[ I = \frac{1}{2} \sum_j m_j z_j^2 \]  

(5)

where \( z_j \) and \( m_j \) are the ion charge number and the molality, respectively.

For the PT measurement, the pK_a value, according to [15], occurs when the titrant volume added is half of the total volume at the Equivalence Point (EP) where pK_a equals pH.

In addition to the PT method, the pK_a value can also be determined by use of Equation (3) together with Equations (6) to (8). It can be seen in Equation (3), if the free amine activity equals the protonated amine activity, thus, pH of the solution is equal to the pK_a value.

\[ n_{Am}^a = n_{Am} + n_{AmH} \]  

(6)

\[ n_{AmH} + n_{H} + n_{Na}^+ = n_{OH}^- + n_{Cl}^- \]  

(7)

\[ K_w = a_{H}^+ a_{OH}^- \]  

(8)

3. Results and Discussion

MEA protonation constant determination was performed at 303K for different ionic strengths \( I \) ranging from 0.01 to 6 mol NaCl/kg water by use of the PT method with 0.1 M H_2SO_4 solution as the titrant. This method has clearly been described by [15].

The pK_a measurement results are presented in Figure 4. It can be seen that the pK_a values increase as the ionic strengths increase. According to [14], this phenomenon occurs due to a salting out effect at high solution ionic strength, resulting in higher pH and pK_a value at the starting point. The effect of the solution ionic strength cannot, therefore, be disregarded.

Based on the Equation (4) by neglecting the short-range VdW forces, the activity coefficients of free MEA (\( \gamma_{MEA} \)) and protonated MEA (\( \gamma_{MEAH^+} \)) will be similar at the same temperature and ionic strength, e.g. \( \gamma_{MEA} = \gamma_{MEAH^+} = 0.77 \) at \( I = 0.1 \) mol/kg water. Thus, the shifted pK_a value is mainly determined by the concentration ratio of MEA and MEAH^+ (see Equation 3). When the concentration of MEA and that of MEAH^+ reach the same value, the solution pH is then equal to the pK_a value, as seen in Figure 5. It can also be seen from the figure that the concentration of MEA decreases as pH decreases while the concentration of MEAH^+ increases as pH decreases. The activity coefficient of MEAH^+ is nearly unity at very low ionic strength and it decreases further as the ionic strength increases.

Furthermore, similar to the activity coefficient, the activity of species has also a similar trend in which the activity of free MEA (\( \alpha_{MEA} \)) decreases as pH decreases and the opposite for the activity of protonated MEA (\( \alpha_{MEAH^+} \)) as shown in Figure 6. In addition, from the figure, it can be seen that the activity of free MEA (\( \alpha_{MEA} \)) decreases as the ionic strength increases at constant pH. This also occurs
on the activity of protonated MEA ($a_{\text{MEAH}^+}$), where the activity of protonated MEA ($a_{\text{MEAH}^+}$) decreases as the ionic strength increases.

![Titration curve of MEA solution](image1)

**Figure 3.** Titration curve of MEA solution ($I = 0.1 \text{ mol/kg water}$) at 303K ($V_e$ = the equivalence point)

![pKa values](image2)

**Figure 4.** pKa values at different ionic strengths at 303K

A similar approach as that in this study has also been used by [19] in which the ionic strengths were evaluated from the salt concentration in the solution. However, this approach might not be appropriate, because the solution ionic strength could be determined not only by the salt concentration but also due to dilution from the titrant as confirmed by [14].
Figure 5. Change in concentration of free MEA and that of protonated MEA along the pH course at $I = 0.1$ mol NaCl/kg water and at 303K

Figure 6. The activity of species at different $I$ at 303K

4. Conclusion
The effect of the ionic strength on the pKa of MEA was measured at different ionic strengths ranging from 0.01 to 6 mol NaCl/kg water at 303K by a potentiometric titration method. The results show that the pKa values, in general, increase as the ionic strengths increase. Moreover, the activity coefficient of species was also determined by the extended Debye-Hückel model. It was observed that the activity of free MEA and that of protonated MEA decrease as the ionic strengths increase at a certain pH.

Acknowledgment
The Chemical Engineering Department, Universitas Islam Indonesia, is acknowledged by the authors for the Research Grant 2017 No: 238/Kajur/10/TK/X/2017 and Prof. I M. Bendiyasa from the Chemical Engineering Department, Universitas Gadjah Mada for the worth discussion.
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