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Amine-based Carbon Dioxide Absorption: Evaluation of Species Activity Coefficient for MEA-H₂O System from 303 to 333K

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Abstract. Acid protonation constant (K_a) is one of the parameters required for thermodynamic modelling. In addition, a rigorous thermodynamic model requires solvent non-ideality properties in order to have a better model representation. This study aims to evaluate species activity coefficients from potentiometric titration data of the MEA-H₂O system at temperatures ranging from 303 to 333K. The results show that the activities of the free MEA and the protonated MEA depend on pH. In addition, the activity coefficients of the protonated MEA determined by the extended Debye-Hückel model were less than unity at different temperatures. This means that the system observed was the non-ideal one.

1. Introduction

The global warming problem has been becoming one of the challenging problems facing the world community. This is caused by the CO_2 emission in the atmosphere which increases annually. Therefore, some parties have been attempting to implement Carbon Capture and Storage (CCS) technology to reduce the CO_2 emission with several scenario options.

Absorption of CO_2 by use of a solvent is a mature technology, however, some researchers have been working on CO_2 capturing solvent development to invent promising solvent candidates, such as alkanolamines, sodium carbonate, amino acid salts (AAS), chilled ammonia, etc. [1-6]. A commercial CO_2 absorbent must fulfil some criteria such as high reaction rate, high net cyclic capacity, low solvent regeneration energy requirement, less corrosive, less volatile, etc. [7-15].

Acid protonation constant (Ka or pK_a) is one of the parameters which is required during kinetic and thermodynamic model developments. The higher the pK_a value of a solvent, the better the solvent performance, because it offers fast kinetic to reduce the dimension of absorption and desorption columns [16]. Aqueous solutions of monoethanolamine (MEA) are the most commonly used as absorbents for the CO_2 absorption. MEA has several advantages compared to other amines, such as high absorption rate, high pK_a, low solvent cost, etc. Determinations of pK_a for the MEA-H₂O system at different temperatures have been reported by [17-22].

A rigorous thermodynamic model requires solvent non-ideality properties, such as species activity coefficients in order to have a better model representation. However, the species activity coefficients data, such as those for the MEA-H₂O system, are still limited in the literature. Therefore, this study aims to evaluate the species activity coefficients from the potentiometric titration data of the MEA-H₂O system at temperatures from 303K to 313K.

2. Activity Coefficient Model

In aqueous solution, a protonated amine will be decomposed into a free amine and a proton. A protonation reaction and its equilibrium constant are written in equations (1) and (2).

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

$$K_a = \frac{a_{Am}\ a_{H^+}}{a_{AmH^+}} \tag{2}$$

where a and subscripts Am and AmH^+ in equation (2) refer to the activity of the species, amine, and protonated amine, respectively. Equation (2) can then be rearranged to get equation (3) as follows:

$$\boldsymbol{pK_a = pH - log\left[\frac{\gamma_{Am}C_{Am}}{\gamma_{AmH^+}C_{AmH^+}}\right]} \tag{3}$$

where γ and c refer to species activity coefficient and concentration, respectively. The species activity coefficient is then determined by the use of the extended Debye-Hückel equation [23] as written in equation (4). This equation had also been used by [11] to evaluate the species activity coefficient for the 2-((2-Aminoethyl) amino) ethanol-water system.

$$\boldsymbol{\ln\gamma_i = \frac{-2.303A_\gamma z_i^2 I^{1/2}}{1+Ba_i I^{1/2}} + 2\sum_j \beta_{ij}m_j} \tag{4}$$

The first term of equation (4) represents the electrostatic forces while the second one represents the Van der Waals (VdW) forces. Since the effect of the VdW forces is insignificant, their contribution can, therefore, be disregarded. The values of A_γ, a_i, and B can be found elsewhere [24, 25]. As seen in equation (4), the species activity coefficient is also ionic strength I dependence where it is defined as follows:

$$\boldsymbol{I = \frac{1}{2}\sum_j m_j z_j^2} \tag{5}$$

where m_j and z_j are the species molality and the ion charge number, respectively.

3. Materials and Method

The materials used in this work were MEA (min. 98 wt.%, Sigma-Aldrich), sulfuric acid (H2SO4, 96.0 wt.%, Merck), and distilled water.

The experimental setup used in this work was similar to that used by [21, 22] which consists of a 300-mL jacketed reactor, a pH meter, a TFA® digital thermometer, a water bath, a digital balance, a magnetic stirrer, and a 5-mL syringe.

About 0.5 g of MEA was added into a beaker glass containing 50 g of distilled water. The solution was then stirred and a certain amount of 0.1 M H_2SO_4 solution was discreetly added into the beaker glass until an equivalence point was reached. The equivalence point can be evaluated graphically by choosing the lowest pH slope or $(d\text{pH}/d\text{V})_{min}$. A detailed procedure can be found elsewhere [21, 22].

4. Results and Discussion

MEA protonation constants were determined at temperatures ranging from 303 to 333K by the use of the potentiometric titration (PT) method. The results can be seen in table 1 in which the pK_a values decrease as the temperatures increase. Based on equation (3), when pH equals pK_a then the activity of free MEA (a_{MEA}) and that of protonated MEA (a_{MEAH^+}) are the same. This is confirmed by the experimental results. As seen in figure 1, the activity of protonated MEA decreases as pH increases, while the activity of free MEA increases as pH increases. These values intersect at pH 9.41 which is similar to the experimental pK_a value at 303K. In addition, if the concentrations of MEA and $MEAH^+$ are plotted, they will intersect at pH 9.53 (see figure 1) and this value is higher than the pK_a value from the experiment. This means that the activity coefficient of $MEAH^+$ is not equal to unity, i.e. non ideal system.

Table 1. Experimental data.

	Temperature (K)			
	303	313	323	333
W_{H2O} (g)	50.0093	50.0180	50.0363	50.0213
W_{MEA} (g)	0.5559	0.3257	0.6057	1.0666
$C_{MEA,0}$ (mol.L^{-1})	0.1807	0.1064	0.1966	0.3432
$m_{MEA,0}$ (mol/kg H$_2$O)	0.1820	0.1066	0.1982	0.3491
Number of data	79	76	89	87
pK_a	9.41	9.18	8.89	8.68
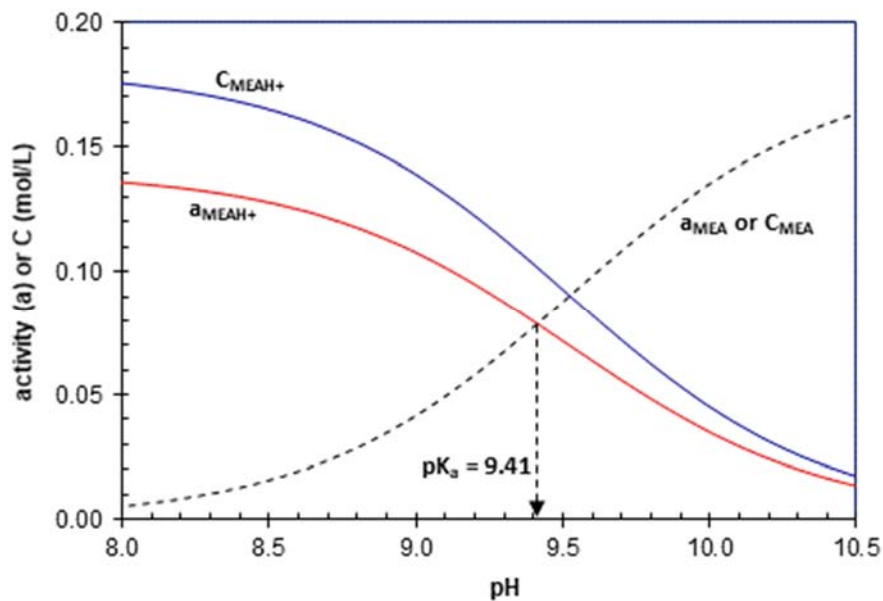
Figure 1. Activities and concentrations of MEA and MEAH$^+$ as a function of pH at 303K.

By neglecting the short-range VdW forces, the activity coefficient of the protonated MEA (γMEAH+) is equal to 0.77 at 303K with the ionic strength of 0.09 (see equation 4). Since the free MEA is a neutral species, its ionic strength will, therefore, be equal to unity (see equation 5). The changes in the activity coefficients and the ionic strengths of the protonated MEA during titration are shown in figure 2. It can be seen from the figure that the activity coefficients of MEAH$^+$ are constant from pH > 4, but they decrease at pH < 4. This occurs because the ionic strengths start to increase as the concentration of ions increases due to dilution of titrant, i.e. H$_2$SO$_4$. This has also been confirmed by [16] in which the solution ionic strength could be determined not only by the salt concentration but also due to dilution from the titrant.

Figure 3 shows the species activities at temperatures from 303 to 333K. It can be seen that the activity of free MEA decreases as pH decreases, but the opposite for the activity of MEAH$^+$. In addition, from the figure, it can also be seen that the intersection between the activity of free MEA and that of MEAH$^+$ gives the pK_a values at different temperatures.
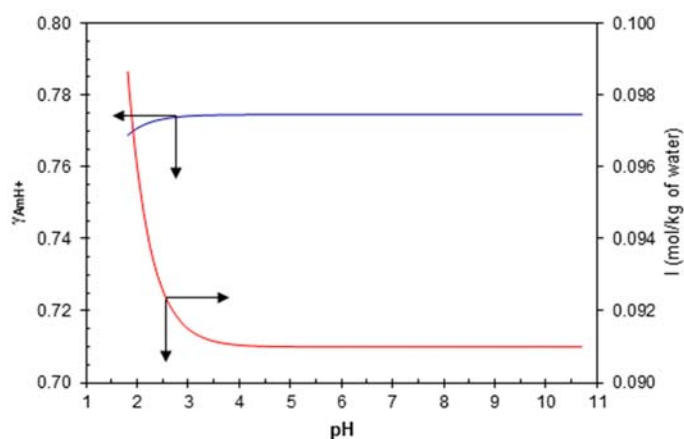
Figure 2. Change in the activity coefficients
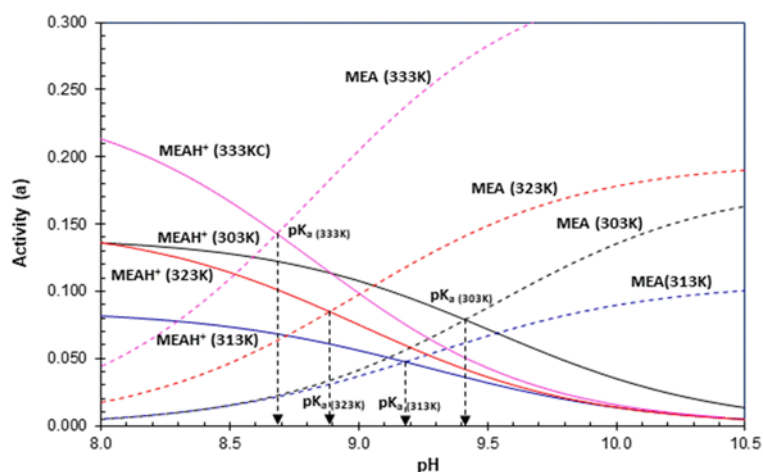and the ionic strengths of MEAH$^+$ as a function of pH at 303K.

Figure 3. The activity of species as a function of pH from 303 to 333K.

5. Conclusion

The pK$_a$ values of MEA were measured at temperatures from 303 to 333K by the PT method. Evaluation of the spices activity for the MEA-H$_2$O system has also been conducted at those temperatures. The results show that the pKa values decrease as the temperatures increase. Moreover, the extended Debye-Hückel model was implemented to determine the species activity coefficients. It was observed that the activity of free MEA increases as pH increases while the activity of the protonated MEA decreases as pH increases.

Acknowledgment

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