Design of protonation constant measurement apparatus for carbon dioxide capturing solvents

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Abstract. Global warming phenomenon has led to world climate change caused by high concentrations of greenhouse gases (GHG), e.g. carbon dioxide (CO$_2$), in the atmosphere. Carbon dioxide is produced in large amount from coal-fired power plants, iron and steel production, cement production, chemical and petrochemical manufacturing, natural gas purification, and transportation. Carbon dioxide emissions seem to rise from year to year; some efforts to reduce the emissions are, therefore, required. Amine-based absorption could be deployed for post-combustion capture. Some parameters, e.g. mass transfer coefficients and chemical equilibrium constants, are required for a vapor-liquid equilibrium modeling. Protonation constant (pK$_a$), as one of those parameters, could then be measured experimentally. Therefore, an experimental setup to measure pK$_a$ of CO$_2$ capturing solvents was designed and validated by measuring the pK$_a$ of acetic acid at 30 to 70 °C by a potentiometric titration method. The set up was also used to measure the pK$_a$ of MEA at 27 °C. Based on the validation results and due to low vapor pressure of CO$_2$ capturing solvents in general, e.g. alkanolamines, the setup could therefore be used for measuring pK$_a$ of the CO$_2$ capturing solvents at temperatures up to 70 °C.

1. Introduction
Removal of carbon dioxide (CO$_2$) is an important industrial operation. Carbon dioxide is produced in large amount from coal–fired power plants, steel production, chemical and petrochemical manufacturing, cement production, natural gas purification, and transportation sectors. The reasons for the CO$_2$ removal are traditionally due to technical and economic concerns [1]. Carbon dioxide present in natural gas will reduce the heating value of the gas. Besides, as an acid gas, CO$_2$ has a potential to cause corrosion in pipes, process equipment, and catalyst poisoning in ammonia synthesis [2]. Natural gas pipe lines usually permit from 1 to 2% CO$_2$ and sometimes as high as 5% [3]. In the past decades, CO$_2$ removal from flue gas streams was mainly deployed for Enhanced Oil Recovery (EOR) operations. Moreover, CO$_2$ was also produced for other industrial applications, such as urea production, carbonation of brine, welding, food and beverage carbonation, dry ice, and soda ash industry [4, 5]. However, environmental concerns, such as the global climate change, are now focused as one of the most important and challenging environmental issues facing the world community, and have motivated intensive research on CO$_2$ capture, utilization, and storage. Carbon dioxide as one of the greenhouse gases (GHG) is currently responsible for over 60% of the enhanced greenhouse effect, while methane (CH$_4$) contributes for 20%, and the remaining 20% is caused by nitrous oxide (N$_2$O), a number of industrial gases, and ozone. Scientific evidence now strongly suggests that increased levels of GHG may lead to higher temperature, and cause climate change on a global scale. Various climate models estimate that the global average temperature may rise by 1.4 to 5.8°C by the year 2100 [1, 6].

A wide range of technologies currently exist for separation and capture of CO$_2$ from gas streams as given by [4]. Such systems have been used in the chemical industry and in the production of technical gases for industrial and laboratory use [7]. In principle, various aforementioned methods could be used for the removal of CO$_2$. Several process–related factors, according to [8], affect the selection of the appropriate method, such as CO$_2$ concentration in the feed stream, nature of other contaminants...
present in the feed stream such as H₂S and water in natural gas, pressure and temperature at which the feed stream is available, product considerations, geographical location, etc. In addition, other criteria that need to consider can also be found in [9]. Therefore, research on solvent development has been conducted intensively, e.g. amino acid salts [10, 11], to meet those criteria.

Absorption can be used for gas separation. It consists of physical and chemical absorptions. The physical absorption is generally favorable at high pressures, i.e. above 5 atm [12], while the latter is vice versa. The chemical absorption is, therefore, more suitable for the CO₂ removal process from exhaust gases where the gas stream is typically at atmospheric pressure.

Amine-based absorption is the most common technology for CO₂ removal today. It is a process with considerable inherent problems, particularly when used on large gas flows, e.g. exhaust from fossil–fuel–fired power stations. The processes are bulky, leading to large investment costs. They have high–energy requirements, and the absorbents in use today are not stable and form degradation products that need to be handled [1]. Aqueous monoethanolamine (H₃NCH₂CH₂OH, MEA), a primary amine, has been used extensively for post combustion CO₂ capturing process. It has several advantages over other commercial alkanolamines, such as high reactivity, low solvent cost, low molecular weight and, thus, high absorbing capacity on a mass basis, and reasonable thermal stability and thermal degradation rate. However, MEA has some drawbacks such as high enthalpy of reaction with CO₂ leading to higher regeneration energy consumption, formation of a stable carbamate and also formation of degradation products with COS or oxygen bearing gases, inability to remove mercaptans, and more corrosive than many other alkanolamines, thus it needs corrosion inhibitors at higher concentrations [13-16].

Mathematical modeling of vapor-liquid equilibria (VLE) is required in designing both absorber and desorber columns. The CO₂-amine-H₂O system is a reactive system where mass transfer and chemical reaction occur simultaneously [17]. To solve the VLE model, some parameters such as mass transfer coefficients and chemical equilibrium constants should be provided. However, some parameters could be determined experimentally and the rest could be regressed from the model. Protonation constant (Kₐ or pKₐ), as one of the parameters, could then be measured experimentally.

The objective of this study is to design an apparatus to measure protonation constants of CO₂ capturing solvents, e.g. alkanolamines. However, the setup should previously be validated by measuring protonation constants of acetic acid (CH₃COOH) at a range of temperatures from 30 to 70 °C by a potentiometric titration method.

1.1. Protonation constant
The protonation constant, also known as the acid dissociation constant, can be calculated from the reaction of a weak acid and a strong base where Kₐ value is equal to the concentration of H⁺ ions in the solution. This occurs when the total volume of titrant added is equal to half of equivalence volume (Vₑ). For a weak acid HA reacting with a strong base BOH, the protonation constant Kₐ can then be expressed as follows [18]:

\[ K_a = \left[ \frac{[H^+][A^-]}{[HA]} \right] \]

Equation (1) indicates that the Kₐ value of the weak acid HA is approximately equal to the concentration of H⁺ ions or the pKₐ equals the pH of the solution.

2. Materials and Method
The materials used in this work consist of glacial acetic acid, sulfuric acid (H₂SO₄), sodium hydroxide (NaOH), MEA, buffer solutions, and distilled water. The acetic acid, NaOH, and H₂SO₄ were obtained from Merck, while MEA was obtained from Sigma-Aldrich. Those chemicals were used without further purification.
Figure 1 shows a designed setup to measure the pKₐ values of CO₂ capturing solvents. It consists of a 300-mL jacketed reactor, a pH meter (Lutron PH-201 with pH electrode PE-03 and accuracy up to 0.01), a TFA³® digital thermometer with accuracy up to 0.1°C, a memmert water bath, an OHAUS³® digital balance with readability up to 0.0001 g, a magnetic stirrer, and a 5-mL syringe.

The setup is designed to determine protonation constants of CO₂ capturing solvents. However, it should previously be validated. The setup validation was conducted by measuring the acetic acid protonation constants at a range of temperatures from 30 to 70 °C by the potentiometric titration method. Moreover, the setup was also tested to measure the pKₐ of MEA at a certain temperature. A similar procedure to determine the pKₐ using the potentiometric titration method can be found elsewhere [18].

3. Results and Discussion

Figure 1 shows the designed setup that shall be validated by measuring the acetic acid protonation constants at 30 to 70 °C by the potentiometric titration method with NaOH 0.1M solution as titrant.

The titration was conducted by discretely adding the titrant into the solution. The amount of the titrant added was calculated from the syringe weight difference. During the titration, there was no temperature rise observed significantly. This occurred due to very little heat that was released during neutralization the acetic acid by NaOH, i.e. 55.2 kJ mol⁻¹ [19]. The titration was terminated after the solution reached pH about 12 in which the solution was in excess of NaOH. This is to ensure that all the acetic acid molecules have reacted with NaOH.

Figure 2 shows the titration results for Run 1 at 30 °C with 8.36 mmoles of acetic acid where the predicted equivalence point was reached at the titrant volume of about 83 mL. It is, however, relatively difficult to determine the precise equivalence point directly from the curve. Another way to determine the equivalence point precisely is, therefore, required. The equivalence point is then determined when the slope (ΔpH/ΔV) gives the highest value. By enlarging the slope around the equivalence point, it can be seen from Figure 3 that the equivalence volume is found to be 82.685 mL. Furthermore, the pKₐ value occurs when the titrant volume equals half of the equivalence volume, i.e. 41.343 mL. At this point, pKₐ is equal to pH and is found to be 4.77. In addition, the setup was also tested by measuring the pKₐ of MEA at 27 °C which was found to be 9.65. The pKₐ of MEA was measured by titrating MEA solution with H₂SO₄ 0.1M as the titrant. A similar procedure was applied to other data and the results together with the literature data are then summarized in Table 1.
Figure 2. Titration curve of acetic acid at 30 °C ($V_e$ = equivalence volume)

Figure 3. Titration slope ($\Delta pH/\Delta V$) of acetic acid at 30 °C
Table 1. pK\textsubscript{a} values of acetic acid at various temperatures

| Run | T (°C) | Number of data | V\textsubscript{e} (mL) | pK\textsubscript{a} | pK\textsubscript{a} from [20] |
|-----|--------|----------------|--------------------------|---------------------|-------------------------------|
| 1   | 30     | 93             | 82.685                   | 4.77                | 4.76                          |
| 2   | 40     | 88             | 82.803                   | 4.78                | 4.77                          |
| 3   | 50     | 93             | 80.980                   | 4.83                | 4.79                          |
| 4   | 60     | 44             | 83.735                   | 4.91                | 4.81                          |
| 5   | 70     | 74             | 78.027                   | 5.00                |                               |
| 6   | 80     | 51             | 87.790                   | 4.94                |                               |
| 11\textsuperscript{a} | 27     | 50             | 62.380                   | 9.65                | 9.44\textsuperscript{b)       |

\textsuperscript{a}MEA, \textsuperscript{b)interpolated from [21]

Figure 4. Comparison of pK\textsubscript{a} values obtained from this work with those from literature

It can be seen from Figure 4 that the pK\textsubscript{a} values of acetic acid obtained from this work, in general, agree with those of [20], except at 70 °C where the data obtained are slightly higher. This might occur due to evaporation loss during titration that took place for some time (approx. 2 hrs). Since the vapor pressure of the acetic acid at 70 °C is relatively high, i.e. 27.6 kPa [22], thus the evaporation loss during titration will significantly reduce the amount of acetic acid in the solution, thereby affecting the measurement result. In case of alkanolamines with somewhat lower vapor pressures, e.g. 1.25 kPa for MEA at 70 °C [22], the evaporation loss during titration might, therefore, be negligible. Based on the validation results, the setup could perform pK\textsubscript{a} measurement of alkanolamines at temperatures up to 70 °C. At higher temperatures than 70 °C, the setup could give high measurement error due to evaporation loss problem.

4. Conclusion
An experimental setup for measuring the protonation constant of CO\textsubscript{2} capturing solvents was designed and validated by measuring the acetic acid protonation constants at 30 to 70 °C by the potentiometric
titration method. The validation results, in general, agree well with the results published in the literature. In addition, the setup was also used to measure the pKa of MEA at 27 °C and the result showed in a good agreement with the published data. The setup could, therefore, be used to measure the protonation constants of CO₂ capturing solvents, e.g. alkanolamines, at temperatures up to 70 °C.

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References
[1] Ma’mun S, Svendsen H F, Hoff K A, Juliussen O 2007 Energy Convers. Manage. 48 251
[2] Astarita G D, Savage W, Bisio A 1983 Gas treating with chemical solvents (New York: John Wiley and Sons)
[3] Buckingham P A 1964 Hydrocarbon Process. 43 113
[4] Rao A B, Rubin E S 2002 Environ. Sci. Technol. 36 4467
[5] Suda T, Iijima M, Tanaka H, Mitsuoka S, Iwaki T 1997 Environ. Prog. 16 200
[6] Williams M 2002 Climate change: Information kit (Geneva: the United Nations Environment Programme and the United Nations Framework Convention on Climate Change)
[7] Desideri U, Corbelli R 1998 Energy Convers. Manage. 39 857
[8] Shaw T P, Hughes P W 2001 Hydrocarbon Process. 5 53
[9] Hoff K A, da Silva E F, Kim I, Grimstvedt A, Ma’mun S 2013 Energy Procedia 37 292
[10] Ma’mun S, Kim I 2013 Energy Procedia 37 331
[11] Ma’mun S 2014 Energy Procedia 51 191
[12] Kohl A, Nielsen R 1997 Gas Purification (Houston - Gulf Publishing Company)
[13] Bucklin R W 1982 Oil Gas J. 11 204
[14] Li Y G, Mather A E 1994 Ind. Eng. Chem. Res. 33 2006
[15] Jou F Y, Mather A E, Otto F D 1995 Can. J. Chem. Eng. 73 140
[16] Liu Y, Zhang L, Watanasiri S 1999 Ind. Eng. Chem. Res. 38 2080
[17] Ma’mun S, Jakobsen J P, Svendsen H F, Juliussen O 2006 Ind. Eng. Chem. Res. 45 2505
[18] Ma’mun S, Kamariah, Sukirman, Kurniawan D, Amelia E, Rahmat V, Alwani D R 2016 SICEST 2016, 9-10 November 2016, Bangka, Indonesia
[19] Jain A K, Singh N B, Das S S 2013 Physical Chemistry Volume 2 (New Delhi - New Age International Ltd.)
[20] Harned H S, Ehlers R W 1933 J. Am. Chem. Soc. 55 652
[21] Bates R G, Pinching G D 1951 J. Res. Natl. Bur. Stand. 46 349
[22] Sinnot R K 2005 Coulson & Richardson’s Chemical Engineering Volume 6 - Chemical Engineering Design (Oxford - Elsevier Butterworth-Heinemann)