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_2O), 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 H_2S 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 CO_2 removal process from exhaust gases where the gas stream is typically at atmospheric pressure.

Amine-based absorption is the most common technology for CO_2 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 ($H_2NCH_2CH_2OH$, MEA), a primary amine, has been used extensively for post combustion CO_2 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 CO_2 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 CO_2-amine-H_2O 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 (K_a or pK_a), 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 CO_2 capturing solvents, e.g. alkanolamines. However, the setup should previously be validated by measuring protonation constants of acetic acid (CH_3COOH) 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 K_a 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 (V_e). For a weak acid HA reacting with a strong base BOH, the protonation constant K_a can then be expressed as follows [18]:

$$K_a = \frac{\left[H^+\right]\left[A^-\right]_{total}}{HA_{left}} \approx \left[H^+\right] \tag{1}$$

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

2. Materials and Method

The materials used in this work consist of glacial acetic acid, sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), MEA, buffer solutions, and distilled water. The acetic acid, NaOH, and H_2SO_4 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 pK_a values of CO_2 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 TFA® digital thermometer with accuracy up to 0.1°C, a memmert water bath, an OHAUS® 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 CO_2 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 pK_a of MEA at a certain temperature. A similar procedure to determine the pK_a using the potentiometric titration method can be found elsewhere [18].
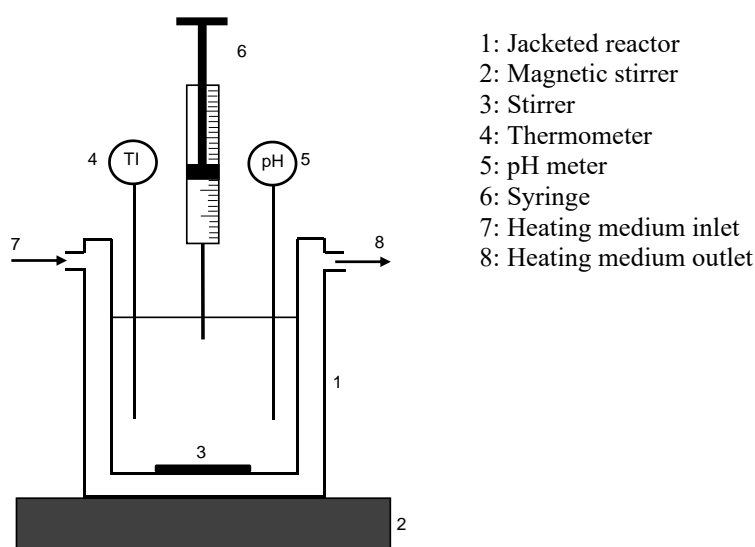

1: Jacketed reactor
2: Magnetic stirrer
3: Stirrer
4: Thermometer
5: pH meter
6: Syringe
7: Heating medium inlet
8: Heating medium outlet

Figure 1. Experimental setup for protonation constant measurements

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 ($\Delta pH/\Delta V$) 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 pK_a value occurs when the titrant volume equals half of the equivalence volume, i.e. 41.343 mL. At this point, pK_a is equal to pH and is found to be 4.77. In addition, the setup was also tested by measuring the pK_a of MEA at 27 °C which was found to be 9.65. The pK_a of MEA was measured by titrating MEA solution with H_2SO_4 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.
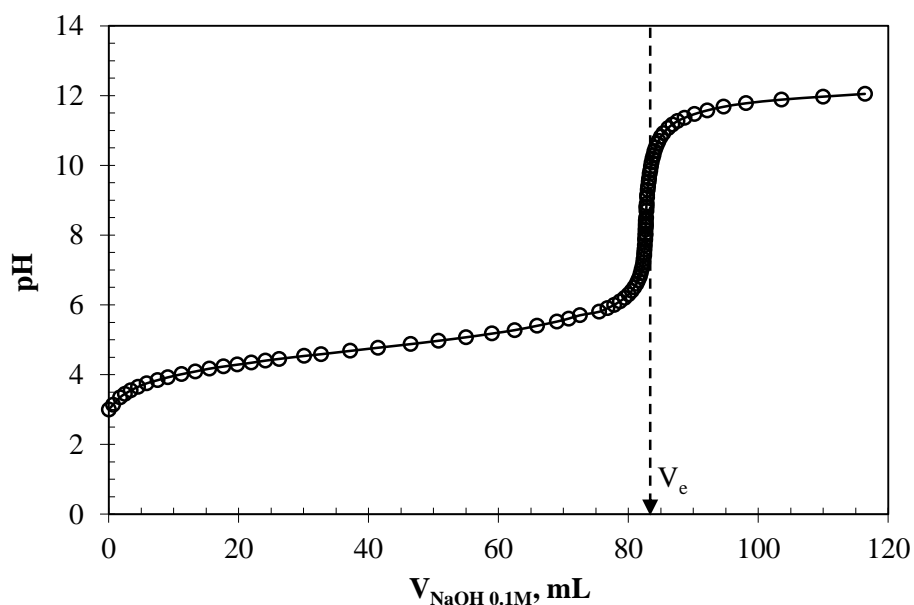
Figure 2. Titration curve of acetic acid at 30 °C (V_e = equivalence volume)
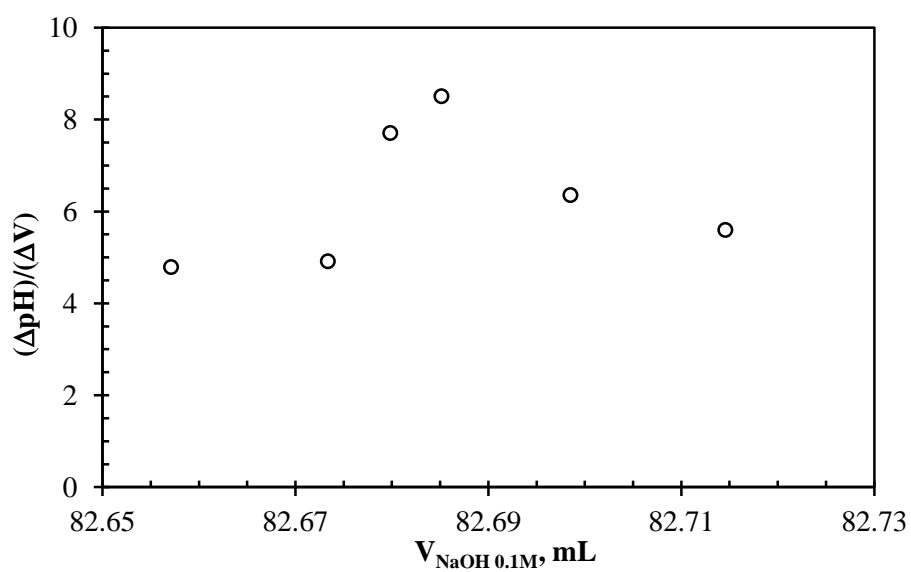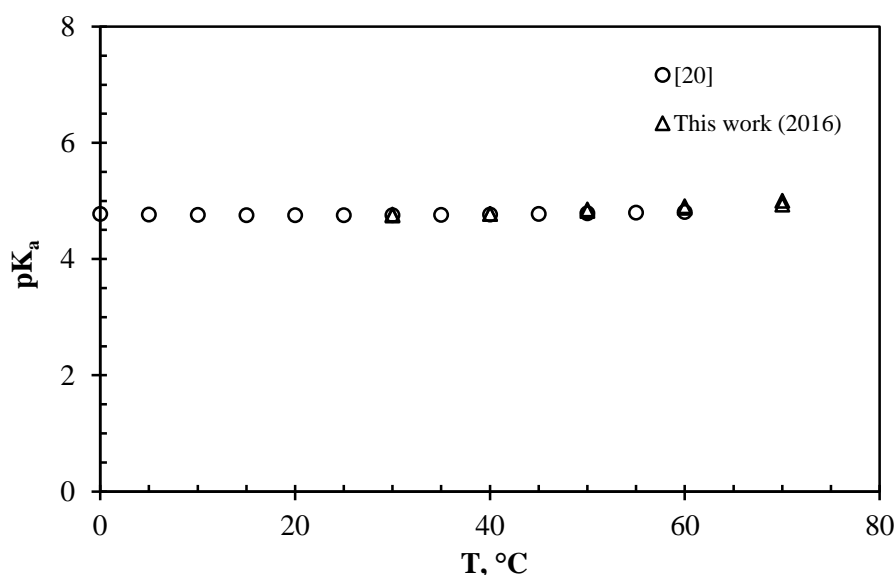

Figure 3. Titration slope ($\Delta pH/\Delta V$) of acetic acid at 30 °C

Table 1. pK$_a$ values of acetic acid at various temperatures

Run	T (°C)	Number of data	V$_e$ (mL)	pK$_a$	pK$_a$ from [20]
1	30	93	82.685	4.77	4.76
2		68	81.302	4.75	
3	40	83	82.803	4.78	4.77
4		60	83.022	4.78	
5	50	93	80.980	4.83	4.79
6		44	83.735	4.86	
7	60	46	83.720	4.91	4.81
8		52	85.960	4.88	
9	70	74	78.027	5.00	
10		51	87.790	4.94	
11[a]	27	50	62.380	9.65	9.44[b]

[a]MEA, [b]interpolated from [21]

Figure 4. Comparison of pK$_a$ values obtained from this work with those from literature

It can be seen from Figure 4 that the pK$_a$ 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$_a$ 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$_2$ 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 CO_2 capturing solvents, e.g. alkanolamines, at temperatures up to 70 °C.

Acknowledgment

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