Research Article

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Determination of alkalinity in the water sample: a theoretical approach

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Abstract: Determination of alkalinity of water sample is generally carried out experimentally by titration method using a proper indicator. In the literature, five different cases of possible alkalinities are reported based on the experimental data of acid titration of water sample using phenolphthalein and methyl orange. The reported data is the volume of acid consumption and the relationship between the alkalinity causing ions present in the water sample. However, no systematic approach is available in the literature to understand these experimentally reported volume of acid utilized for neutralization reaction. To make students understand the key features of the reported experimental data, a systematic approach is presented in this study. By using a simple mathematics and a theoretical explanation to the reported reactions taking place during acid titration of water sample, a supplementary document is developed. The theoretical concept in the form of supplementary information is introduced without altering any data reported in the literature or experimental procedure.

Keywords: alkalinity; experimental; supplementary; theoretical; titration; water technology

1 Introduction

Water Technology is included in first year engineering chemistry syllabus. The course content includes topics on determination of alkalinity of water, five different cases of probable type of alkalinities presented as an experimental data, numerical and laboratory session. The experimental data presented in the course is based on the titration of water sample given as the relationship between the type of ions and alkalinity as a function of volume of acid utilized for neutralization.

However, many students were finding it difficult to interpret and understand the concept behind the data presented. This impeded their understanding and conceptual approach towards the concept which was reflected from their performance in class room interaction. To make teaching and learning effective, the concept was approached in a different way and presented before the students as supplementary information. This inquiry-based approach strategy was used to facilitate student's scientific learning and the performance was evaluated based on the traditional teaching and assessment approach.

1.1 Water alkalinity and its determination

Alkalinity is one of the important characteristics of water, which is a measure of the ability of water to neutralize the acid. It is observed that the alkalinity of the water is primarily due to the presences of bicarbonates, carbonates and hydroxides of sodium, potassium, calcium and magnesium. Depending upon the ions present, the alkalinity can be classified as caustic alkalinity (due to OH^- and CO_3^{2-} ions) and bicarbonate alkalinity (due to HCO_3^- ions) (Gray, 2017 pp. 44–46; Hammer & Hammer, 2013 pp. 17–18; Maiti, 2004 pp. 33–37; Manahan, 2010 p. 56; Patton, 1991, pp. 23–29).

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Estimation of alkalinity due to different ions is based on the titration of the water samples against a standard acid (e.g. sulphuric acid) making selective use of an indicator (Hammer & Hammer, 2013, pp. 17–18). Typical indicators used are phenolphthalein and methyl orange. The volume of acid consumed during the titration can be used to determine the strength of various alkalinity causing ions.

The typical analytical procedure to estimate the alkalinity of water makes use of well-established and documented acid-base titration method that involves following steps.

Step 1

- A known volume of water sample is pipette out into a conical flask to which 2 to 3 drops of phenolphthalein indicator is added. Depending upon the type of alkalinity present the water sample will either remain colorless or will turn pink. If no cooler is produced, phenolphthalein alkalinity is not present.
- If the solution turns pink, titrate water sample with standard H_2SO_4 solution taken in a burette until the pink colour disappears or the pH of the solution is 8.3.
- Record the volume of acid consumed (Burette reading) as ‘P’ mL.

Step 2

- To the same sample add 2 to 3 drops of methyl orange indicator. The colour of the solution will turn orange.
- Continue titration until the colour changes from orange to pink or the pH of the solution is 4.5.
- Record the total volume of acid consumed as “M” mL or “T” mL.
- Repeat the above procedure (Step 1 and Step 2) to get concordant values.

Using the mean values of volume of acid consumed obtained in step 1 and step 2 respectively, the type and amount of alkalinity expressed in mg/L of $CaCO_3$ is calculated using following equation:

$$\text{Alkalinity}\ (\text{mg/L as CaCO}_3) = \frac{\text{volume of acid consumed}\ (\text{mL}) \times \text{molarity of acid}\ (\text{M}) \times 50 \times 1000}{\text{volume of water sample}\ (\text{mL}).}$$

The typical alkalinity titration curve (pH versus volume) for a hydroxide-carbonate system showing two points of inflections that corresponds to phenolphthalein alkalinity (Step 1) and total alkalinity (Step 2) is shown in Figure 1 [Maiti, 2004 p. 34]. At first point of inflection (pH 8.3), de-colourization of phenolphthalein indicator indicates complete neutralization of OH^- and ½ CO_3^{2-}. At second inflection point (pH 4.5), de-colourization of methyl orange indicator indicates complete neutralization of ½ CO_3^{2-} and HCO_3^-.

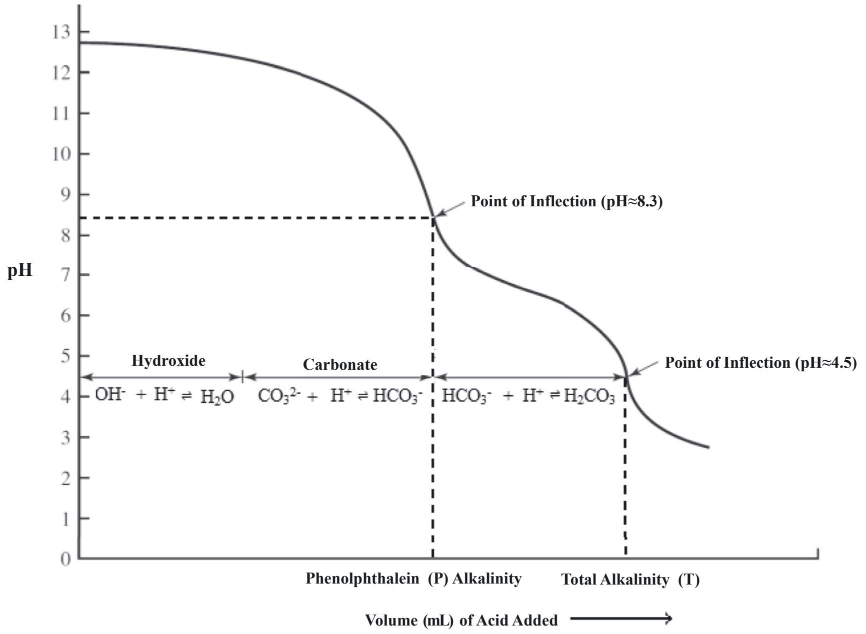

Figure 1: Typical acid titration curve for hydroxide carbonate system.

The reactions taking place during titration (Manahan, 2010, p. 56) and their corresponding equilibrium expression at 25 °C are represented by following equations (Frank, 2004, pp. 246–247; Hammer & Hammer, 2013, pp. 12):

(a) $OH^- + H^+ \rightleftharpoons H_2O$, $K_a = [H^+][OH^-]/[H_2O] = 1.0 \times 10^{-14}$

(b) $CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$, $K_b = [H^+][CO_3^-]/[HCO_3^-] = 4.7 \times 10^{-11}$

(c) $HCO_3^- + H^+ \rightleftharpoons CO_2 + H_2O \rightleftharpoons H_2CO_3$, $K_c = [H^+][HCO_3^-]/[H_2CO_3] = 4.8 \times 10^{-7}$

Note that dissolved CO_2 in water is represented as H_2CO_3 by equation (d) and the equilibrium constant is expressed as follows:

(d) $CO_2(aq) + H_2O \rightleftharpoons H_2CO_3$ $K_d = [H_2CO_3]/[P_{CO_2}] = 4.48 \times 10^{-5}M$

The volume of acid used up to phenolphthalein end point corresponds to the complete neutralization of hydroxide ion (reaction a) and half-neutralization of carbonate ions (reaction b) and is known as phenolphthalein (P) alkalinity (Manahan, 2010, p. 56; Patton, 1991, pp. 23–29). The volume of acid used up to methyl orange end point corresponds to the reaction (a), (b) and (c) i.e. complete neutralization of hydroxide, carbonate and bicarbonate ions and is known as total (T) alkalinity (Manahan, 2010, p. 56; Patton, 1991, pp. 23–29). Once the phenolphthalein and total alkalinities are determined, the types of alkalinity can be due to different ions and their relationship is estimated using the experimental data reported in Table 1 (Maiti, 2004, pp. 33–37).

1.2 Students learning difficulties

When this topic was introduced in the class room teaching, it was observed that students were not able to understand, visualize and apply the concept to the data reported in Table 1. The major problems identified during class room interaction that were associated with learning this topic and understanding Table 1 were: (i) they were not able to identify the type of alkalinity present in water sample and correlate with their relationship, (ii) Unable to explain the meaning all five cases, (iii) Unable to understand why phenolphthalein (P) alkalinity is related to 1/2 times methyl orange or total (T) alkalinity, (iv) Unable to visualise half reaction between carbonate ion and H^+ ion during phenolphthalein (P) alkalinity and (iv) unable to evaluate the distribution of total volume of acid utilize among the different ions at the end of titration. They were also found to memorise Table 1 instead of applying it conceptually.

1.3 Strategy adopted for effective learning

To overcome learning difficulties, no systematic approach was available in the literature to understand these experimentally reported volumes of acid utilized for neutralization reaction as per author's knowledge. Therefore, for easy understanding and application of concept to water technology supplementary information was

Table 1: Alkalinity due to different ions and their relationship.

Case no	Results of titration	Amount of OH^- alkalinity	Amount of CO_3^{2-} alkalinity	Amount of HCO_3^- alkalinity
Case 1	P = 0	Absent	Absent	T
Case 2	P = T	T	Absent	Absent
Case 3	P = 1/2 T	Absent	2P	Absent
Case 4	P > 1/2 T	2P–T	2 [T–P]	Absent
Case 5	P < 1/2 T	Absent	2P	T–2P

developed by applying a simple mathematical approach to Table 1. The supplementary information developed was presented in class room teaching and the performance outcome of students was evaluated by performing assessments in terms of class test (theory, numerical and quiz) and practical's. A systematic theoretical approach for each case reported in Table 1 along with students learning assessments and outcomes is discussed.

2 Theoretical discussion

Case 1, P = 0

When phenolphthalein alkalinity (P) is zero, it is an indication that the water sample will not turn to pink colour on the addition of phenolphthalein indicator. Thus, we can say that the ionic species which are responsible for phenolphthalein alkalinity is absent.

$$\text{i.e. P} = \text{OH}^- + ½\ \text{CO}_3^{2-} = 0 \tag{1}$$

Now, to determine the methyl orange or total alkalinity, methyl orange indicator is added to the water sample. The water sample turns to orange colour. On titration with acid, the total alkalinity of water sample is represented as

$$\text{T} = \text{OH}^- + \text{CO}_3^{2-} + \text{HCO}_3^-\ (\text{Originally present}) \tag{2}$$

Putting, P = 0 in equation (ii) we get,

$$\text{T} = \text{HCO}_3^-$$

Therefore, the volume of acid utilized is only for the neutralization of bicarbonate ions that are originally present in the water sample.

$$\text{i.e HCO}_3^-\ (\text{Originally present}) + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3 \tag{3}$$

Thus, alkalinity of water in terms of $CaCO_3$ equivalent is given by

$$\text{Alkalinity due to HCO}_3^- = \frac{\text{T} \times \text{molarity of acid} \times 50 \times 1000}{\text{volume of water sample}}$$

Case 2, P = T

The situation, where phenolphthalein alkalinity (P) is equal to total alkalinity is only possible when the water sample contains no ionic species that can be detected by methyl orange indicator during titration with an acid.

Thus, the ionic species which are responsible for phenolphthalein alkalinity are represented as.

$$\text{P} = \text{OH}^- + ½\,\text{CO}_3^{2-} \tag{4}$$

and the absence of methyl orange alkalinity is represented as

$$\text{T} = \text{OH}^- + \text{CO}_3^{2-} + \text{HCO}_3^-\ (\text{Originally present}) = 0 \tag{5}$$

Since, no methyl orange alkalinity is present, it indicates that the HCO_3^- (generated) by half-neutralization reaction of CO_3^{2-} is also absent.

$$\text{i.e CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^-\ (\text{generated})\ \text{is absent} \tag{6}$$

This implies absences of carbonates (CO_3^{2-}) in the water sample.

Therefore, equation (4) becomes P = OH^-, which is the theoretical volume of acid consumed for neutralization of OH^- only.

$$\text{i.e OH}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O} \tag{7}$$

Thus, alkalinity of water in terms of $CaCO_3$ equivalent is given by.

$$\text{Alkalinity due to OH}^- = \frac{\text{P} \times \text{molarity of acid} \times 50 \times 1000}{\text{volume of water sample}}$$

Case 3, P = ½ T or 2P = T

The situation, where phenolphthalein alkalinity (P) is equal to half of total alkalinity indicates that the volume of acid consumed for the first end point and the corresponding second end point of the titration is exactly same. This is only possible if OH^- and HCO_3^- (originally present) are absent in the water sample.

$$\text{i.e P} = \text{OH}^- + \tfrac{1}{2}\,\text{CO}_3^{2-} = 0 + \tfrac{1}{2}\,\text{CO}_3^{2-} \tag{8}$$

and

$$\text{T} = \text{OH}^- + \text{CO}_3^{2-} + \text{HCO}_3^- \;(\text{Originally present}) = \text{CO}_3^{2-} \tag{9}$$

Thus, for the first end point of the titration with phenolphthalein indicator we have,

$$\text{i.e CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^- \,(\text{Generated}) \tag{10}$$

and for the second end point of the titration with methyl orange indicator we have,

$$\text{HCO}_3^- \;(\text{Generated}) + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3 \tag{11}$$

Therefore, above reactions indicates that exactly same moles of H^+ are consumed satisfying the condition $2P = T = CO_3^{2-}$, which is the theoretical volume of acid consumed for neutralization of CO_3^{2-} only.

Thus, alkalinity of water due to CO_3^{2-} in terms of $CaCO_3$ equivalent is given by,

$$\text{Alkalinity due to CO}_3^{2-} = \frac{2\text{P} \times \text{molarity of acid} \times 50 \times 1000}{\text{volume of water sample}}$$

Case 4, P > 1/2 T

For the situation, where phenolphthalein alkalinity (P) is greater than half the total alkalinity indicates that the volume of acid required for the first end point is greater than second end point of the titration.

Thus, one can assume that HCO_3^- (originally present) is absent in water sample and the alkalinity of water is due to OH^- and CO_3^{2-} only.

For the first end point of the titration with phenolphthalein indicator we have,

$$\text{i.e} \quad \text{P} = \text{OH}^- + \tfrac{1}{2}\,\text{CO}_3^{2-} \tag{12}$$

Rearranging equation (12) we have

$$2\text{P} = 2\text{OH}^- + \text{CO}_3^{2-} \tag{13}$$

And for the second end point of the titration with methyl orange indicator we have,

$$\text{T} = \text{OH}^- + \text{CO}_3^{2-} + \text{HCO}_3^- \;(\text{Originally present})$$

Since, HCO_3^- (Originally present) = 0.

We have,

$$\text{T} = \text{OH}^- + \text{CO}_3^{2-} \tag{14}$$

Subtracting equation (13) and (14), we get $2P–T = OH^-$

Which is the theoretical volume of acid consumed for neutralization of OH^-only = 2P–T

$$\text{i.e OH}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O} \tag{15}$$

Thus, alkalinity of water due to OH^- in terms of $CaCO_3$ equivalent is given by,

$$\text{Alkalinity due to OH}^- = \frac{(2\text{P} - \text{T}) \times \text{molarity of acid} \times 50 \times 1000}{\text{volume of water sample}}$$

Now,

Putting value of $OH^- = 2P - T$ in equation (14) we get.

$$T = (2P - T) + CO_3^{2-} \text{ or } \quad CO_3^{2-} = 2(T - P)$$

which is the theoretical volume of acid consumed for neutralization of CO_3^{2-} only = 2 (T–P)

$$\text{i.e } CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \text{ (Generated)} \tag{16}$$

And

$$HCO_3^- \text{ (Generated)} + H^+ \rightleftharpoons H_2CO_3 \tag{17}$$

Thus, alkalinity of water due to CO_3^{2-} in terms of $CaCO_3$ equivalent is given by,

$$\text{Alkalinity due to } CO_3^{2-} = \frac{2(T - P) \times \text{molarity of acid} \times 50 \times 1000}{\text{volume of water sample}}$$

Case 5, P < 1/2 T

For the situation, where phenolphthalein alkalinity (P) is less than half the total alkalinity indicates that the volume of acid required for the first end point is lesser than second end point of the titration.

Thus, one can assume that OH^- is absent in water sample and the alkalinity of water is due to CO_3^{2-} and HCO_3^{2-} only.

For the first end point of the titration with phenolphthalein indicator we have,

$$P = OH^- + ½\, CO_3^{2-} \tag{18}$$

Since, $OH^- = 0$

We have,

$$2P = CO_3^{2-} \tag{19}$$

Which is the theoretical volume of acid consumed for neutralization of $CO_3{}^{2-}$ only = 2P.

$$\text{i.e } CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \text{ (Generated)} \tag{20}$$

Thus, alkalinity of water due to CO_3^{2-} in terms of $CaCO_3$ equivalent is given by,

$$\text{Alkalinity due to } CO_3^{2-} = \frac{2P \times \text{molarity of acid} \times 50 \times 1000}{\text{volume of water sample}}$$

And for the second end point of the titration with methyl orange indicator we have,

$$T = OH^- + CO_3^{2-} + HCO_3^- \text{ (Originally present)} \tag{21}$$

Or

$$T = CO_3^{2-} + HCO_3^- \tag{22}$$

Putting value of $2P = CO_3^{2-}$ in equation (22) we get.

$$HCO_3^- = T - 2P$$

Which is the theoretical volume of acid consumed for neutralization of HCO_3^- only = T–2P.

$$HCO_3^- \text{ (Generated)} + H^+ \rightleftharpoons H_2CO_3 \quad \text{and} \quad HCO_3^- \text{ (Originally present)} + H^+ \rightleftharpoons H_2CO_3$$

Thus, alkalinity of water due to CO_3^{2-} in terms of $CaCO_3$ equivalent is given by,

$$\text{Alkalinity due to } HCO_3^- = \frac{(T - 2P) \times \text{molarity of acid} \times 50 \times 1000}{\text{volume of water used}}$$

3 Learning assessments

In order to measure the understanding of the students towards the introduction of supplementary information developed, learning assessments in terms of class test and practical test were carried out.

3.1 Class room session

A class test that includes theory, numerical and quiz comprising of 20 marks each (total 60 marks) was conducted to assess the level of understanding of theoretical concept. The questions were designed taking into consideration the Bloom's taxonomy levels (knowledge, comprehension, application, analysis, evaluate and create) for students learning assessment.

3.2 Laboratory session

For laboratory session two practical tests were conducted each of 20 marks (total 40 marks). For the test two water samples were prepared in laboratory that meet case 4 and case 5 of Table 1, respectively. For case 4 the water sample comprise of calculated amount of NaOH and Na_2CO_3 in one litre water, while for case 5 the water sample comprise of calculated amount of Na_2CO_3 and $NaHCO_3$ in one litre water. The titrant used was 0.01 M HCl. Students were instructed to follow the titration procedure to identify the type and calculate the amount of alkalinity.

For both class test and practical test a threshold of 95 percentage mark was set. Therefore, number of students out of total 120 students scoring 57 marks in class test and 38 marks in practical test was set as criteria for evaluation. Finally, the percentage of attainment level in terms of learning outcome was determined using following relation.

$$\text{Percentage learning outcome} = (0.6\,\text{X}\,a + 0.4\,\text{X}\,b)$$

where, a = percentage of students scoring ≥ threshold of 95 % marks in class test out of 60. b = percentage of students scoring ≥ threshold of 95 % marks in practical test out of 40.

A schematic of learning assessment strategy adapted to evaluated learning outcome is shown in Figure 2.

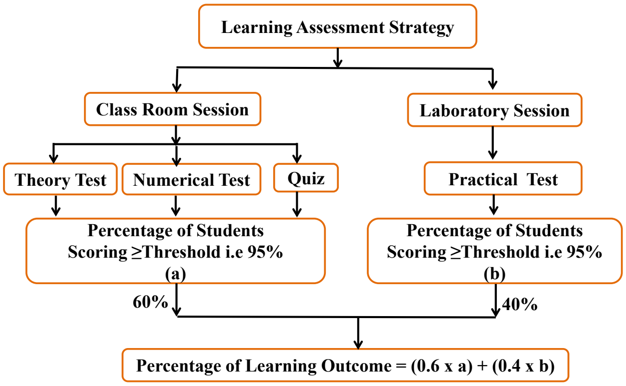

Figure 2: Schematic showing assessment strategy and learning outcome evaluation.

3.3 Learning outcomes

Total 120 students were introduced with the supplementary material in both class room and laboratory session. The impact of this supplementary information on conceptual understanding and learning ability of the students was monitored by traditional teaching and assessment tools like class room interaction, subject concentric class test, quiz, assignments, numerical solving and laboratory sessions. The percentage learning outcome obtained was 95 % indicating that the use of this supplementary material had a profound impact on understanding the key features of experimental data reported in Table 1. Students were able to explore and demonstrate better understanding for analysis of water by the combination of experimental and theoretical approach. In both, class room teaching and laboratory session, students were able to easily identify alkalinity due to different ions and their relationship. Using the theoretical description as a supplementary material presented in this study, students were able to deduce the theoretical volume of acid required for neutralization. This was reflected by the ease with which students were able to solve numerical on determination of water alkalinity.

4 Conclusions

A systematic theoretical description using simple mathematics applied to the chemical reaction for water alkalinity determination was presented to first year engineering students as a part of chemistry curriculum on water technology. Based on the overall assessment of the student's response in both class test and practical test, it might be suggested that the supplementary information has an innovative reform on understanding the concept and learning ability of the students.

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