Developing Methods for Proper Determination of Alkalinity in Oil and Gas Field Brines

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Abstract

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Developing Methods for Proper Determination of Alkalinity in Oil and Gas Field Brines

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The objective of this research is to investigate and develop methodologies to analyze brine chemistry data and to extract useful information that can be applied to corrosion modeling. The research work covers guidelines on how to interpret field brine chemistry data, methods to conduct titrations of unknown brines, and the development and validation of a model predicting titration curves over a wide range of bicarbonate and carboxylate ions, and salt concentrations. The influence of carboxylate salts, sparging samples with CO_2, and ionic strength on the analysis of titration curves are discussed. Issues associated with pH 4.5 endpoints used throughout the industry in water chemistry analysis, as they apply to samples containing carboxylate salts, are discussed. Water chemistry analyses from field data are reviewed to update current methodologies so that they are of more practical use for corrosion engineers in the industry. The findings will influence the interpretation of water chemistry documentation, and the corresponding inputs into MULTICORP^{TM}, as well as other software packages, for corrosion prediction.

Dedication

I dedicate this work to the people who have provided guidance and pushed me to be the best person I can be. Do the best you can every day, no one can ask anymore of you.

Acknowledgments

I would like to thank my advisor Dr. Marc Singer for all of his guidance and expertise. I would also like to thank Dr. Bruce Brown, Dr. David Young, Dr. Huizinga and David Blumer for their expert guidance, continuous encouragement and patience. A special thanks to the staff and students at the Institute for Corrosion and Multiphase technology for providing a wonderful work environment.

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Chapter 1: Introduction

The entire world economy is still largely based on fossil fuels, from the gasoline and diesel needed to propel vehicles, bitumen for highways and construction, the natural gas required to produce electricity and heat homes, or the hydrocarbon base materials used to produce polymers. Safe extraction of petroleum from underground reservoirs is key in maintaining current levels of travel and production of consumer goods. Transmission of raw petroleum products is mainly done through pipelines made of carbon steel, which is prone to corrode in the presence of water. It is estimated that the cost of corrosion globally is approximately \$2.5 trillion dollars per year, which is 3.4% of the Gross Domestic Product (GDP) [1]. Accurate corrosion estimation is important for assuring integrity of oil and gas wells and pipelines, appropriate material selection choices during any design phase, economic mitigation strategies, and to ensure environmental protection. The area of corrosion science that is discussed in this research is related to the first step in any corrosion risk assessment associated with hydrocarbon extraction: the determination of water chemistry of oilfield brines (aqueous solution with high salt content). Some models and methods have been proposed to characterize water speciation but they are not widely used in the industry, mainly due to their inherent complexity which often leads to misinterpretation of results. This research work aims at clarifying these misunderstandings associated with the interpretation of water chemistry analysis from oilfield brines, outlines the development of a clear methodology on how to determine alkalinity, and presents a coherent way forward on how to correctly use this information in corrosion prediction.

Chapter 2: Background

2.1 Oil and Gas Field Brines

Oil and gas fields are large underground zones from which petroleum is extracted. During the process of extracting oil and gas, significant quantities of water are always produced. The amount and composition of produced water typically depend both on the life of the well (*i.e.* production history) and its specific geological formation. The produced water is referred to as oil field brine or just brine [2]. Produced water contains many different species including high concentrations of dissolved salts and organic acids. Produced water also contains dissolved CO_2 and H_2S species from reservoir conditions, and the corresponding carbonic and sulfide species [3]. Species present in produced water are characterized by the use of water chemistry analytical techniques. The generated information is crucial in assessing the corrosivity of brines. However, water chemistry data reported in brine characterization documentation can be misleading and are often misinterpreted. This in turn generates many challenges in evaluating the risk of corrosion in oil and gas transmission pipelines.

2.2 Corrosion of Mild Steel

Corrosion is an electrochemical process that occurs through two sets of coupled electrochemical half-reactions involving a metal and its environment. The two half-reactions are known as the anodic and cathodic reactions, where the oxidation reaction occurs at the anode and reduction occurs at the cathode. The anodic dissolution of iron, which translates into metal loss, occurs *via* Reaction 1.

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \qquad \text{Reaction 1}$$

The main cathodic reaction is the reduction of hydrogen ions at the metal surface to form hydrogen gas *via* Reaction 2.

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2\,(g)} \qquad \text{Reaction 2}$$

The overall reaction can be expressed by adding the cathodic reaction to the anodic reaction, as shown in Reaction 3.

$$Fe_{(s)} + 2H^+_{(aq)} \rightarrow Fe^{2+}_{(aq)} + H_{2\,(g)} \qquad \text{Reaction 3}$$

Acidic conditions often exist in oil and gas brines due to the presence of carbonic acid, which is derived from the dissolution and hydration of carbon dioxide, and carboxylic acids, such as acetic acid, in the aqueous phase [4].

2.3 Fundamentals of Aqueous Speciation and Corrosion in CO_2 Environments

Low alloy carbon steels, which are essentially comprised of iron and small amounts of alloying elements, can corrode in the presence of an aqueous phase. In the oil and gas industry, the main source of corrosion is due to the presence of gaseous CO_2 which dissolves in water to form a weak acid: carbonic acid [5]. The dissolution of carbon dioxide in water is represented in Reaction 4 seen below.

$$CO_{2\,(g)} \rightleftharpoons CO_{2\,(aq)} \qquad \text{Reaction 4}$$

Dissolved CO_2 then hydrates to form carbonic acid following Reaction 5.

$$CO_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3\,(aq)} \qquad \text{Reaction 5}$$

Carbonic acid (H_2CO_3) then dissociates through two steps shown in Reaction 6 and Reaction 7.

$$H_2CO_{3\,(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3\,(aq)} \qquad \text{Reaction 6}$$

$$HCO_{3\,(aq)}^{-} \rightleftharpoons H_{(aq)}^{+} + CO_{3\,(aq)}^{2-} \qquad \text{Reaction 7}$$

CO_2 corrosion of carbon steel involves electrochemical and chemical reactions, as stated in the previous section, and mass transfer processes. The overall rate of a series of sequential reactions is always controlled by the speed of the slowest step. If the slowest step is a chemical reaction, it can significantly alter the rate of electrochemical processes at the surface, and consequently the rate of corrosion [4]. The main way the presence of H_2CO_3 increases the corrosion rate is through its dissociation into aqueous hydrogen and bicarbonate ions in Reaction 6. The pK_a of this reaction is located at 6.4 at 25°C – this represents the pH for which the concentrations of H_2CO_3 and HCO_3^- are equal. This reaction serves as an additional source of H^+ ions replenishment, which promotes the main reduction reaction shown in Reaction 2. The direct reduction of H_2CO_3 has also been postulated by several researchers [6][7][8] to account for the increase of the corrosion rate but this mechanism has been recently considered as insignificant in tested conditions (acidic pH) [9]. This leads to the main effect of carbonic acid being to replenish the supply of hydrogen ions as they are consumed by the reduction reaction. This mechanism creates what is referred to as a “buffering effect” and can be described by the dissociation reactions shown in Reaction 6 and Reaction 7. The understanding of the dissolution of CO_2(g) in water to form aqueous CO_3^{2-}(aq), HCO_3^-(aq), and H_2CO_3(aq) is crucial in the study of corrosion [10].

Other species that are found in produced waters are sulfides and organic acid species. The dissolution of acetic acid, the most common type of organic acids found in brines, in water is represented in Reaction 8 below. The pK_a of this reaction is located at 4.8 at 25°C, the pH where the concentrations of CH_3COOH and CH_3COO^- are equal.

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)} \qquad \text{Reaction 8}$$

Acetic acid dissociation also contributes to the corrosion of mild steel by contributing to this “buffering effect”. The dissociation of the acetic acid replenishes the hydrogen ions used in Reaction 2, however this affect does not overwhelm the corrosion influence of carbonic acid until concentrations are in excess of 50 ppm_w [11].

Sulfide species are also expected to be present at *in situ* conditions but are not included in the scope of the present study.

Since directly measuring pH and CO_2 species concentrations in produced water is extremely difficult at operating conditions, engineers often rely on calculations and predictive software to assess the corrosivity of the fluids. Developing a solid understanding of water speciation is consequently essential. Produced water is often made of a complex brine containing not only dissolved carbonic species but also a variety of salts which can affect the pH. This overall aspect is commonly represented by the value of alkalinity which is always a conserved value regardless of the operating conditions. This means that the value of alkalinity is the same at the inlet and outlet of a pipeline (unless significant water condensation or release of Fe^{2+} from corrosion occurs). Field brines frequently exist with high concentrations of dissolved salts that contribute to non-ideality, where activity coefficients should be incorporated to account for the nonideality present in solution when predicting pH.

2.4 Activity Coefficients

The activity of a chemical species is thought of as the measure of effectiveness for reaction where the activity coefficient is multiplied by the concentration of species. In an ideal condition the activity coefficient is assumed to be one. The use of an activity coefficient is similar to fugacity representing the effectiveness of a set partial pressure of a gas. The species placed in the aqueous phase interact with each other, interactions between them becoming significant at higher concentration. The species interactions change the activity depending on the concentration of the ionic species and, hence, on the ionic strength of the solution. This causes an increase or decrease in the activity depending on the species. The value of the activity coefficients is also known to change with pH as pH is associated with the concentration of H^+ in solution. In this research, activity models were not studied in great detail but species activities were used when appropriate and extracted from already existing models. Two of these existing models that can be considered for calculating activity coefficients are the Pitzer activity model and the Mixed Solvent Electrolyte model (MSE). The Pitzer activity model is probably the most commonly adopted model to account for chemical and electrostatic forces and has been implemented in Ohio University downhole corrosion prediction software WELLCORP™ [12], [13], [14]. The Mixed Solvent Electrolyte model (MSE) is a more recent, and more comprehensive model – some aspects of this model have been implemented in Ohio University pipeline corrosion prediction software MULTICORP™. The Pitzer and Mixed Solvent Electrolyte models are both very complex activity-based models. A simpler model often considered to generate activity coefficients is known as the Debye-Hückel model. The Debye-Hückel equation is shown below in Equation 1. The coefficients of 0.509 and 3.28 are applicable for solutions at 25℃ [15]

$$-log\gamma_A = \frac{0.509\ Z_A^2\sqrt{I}}{1 + 3.28\alpha_A\sqrt{I}} \qquad \text{Equation 1}$$

γ_A = Activity coefficient of species *A*

Z_A = Charge on species *A*

I = ionic strength of the solution (M)

α_A = The effective diameter of the hydrated ion (nm)

The Debye-Hückel model assumes that all species of similar charge will have the same activity coefficients. The Debye-Hückel model is also intended to be used with dilute solutions, not to exceed 0.2 M. The MSE and Pitzer models are both intended to be used at much higher ionic strengths. Activity coefficients used in this research were calculated using OLI software which uses the MSE model [16]. A table of these activity coefficients obtained from the MSE model in OLI can be found in Table 13-Table 15 of the appendix.

2.5 Alkalinity

Alkalinity is a measure of the capacity of an aqueous solution to resist acidification. It is dependent on the presence of ionic species in water, such as HCO_3^- , CO_3^{2-}, Na^+, Cl^- and OH^-, yet, as the solution composition becomes more complicated, the number of ions involved increases. Alkalinity is also referred to as the buffering capacity of a water sample and a measure of the ability of that water sample to neutralize acids and maintain a fairly stable pH level. Water with a high alkalinity will experience less of a change in its acidity when exposed to changes in the environment. Acidity is measured through pH, which is linked to the activity of H^+ in solution. As mentioned earlier, knowing the alkalinity of brines is essential for predicting water speciation in production conditions, which in turn affects the processes of corrosion and corrosion product precipitation in solutions. In brines containing dissolved CO_2, alkalinity can be expressed as Equation 2, which is based on the electroneutrality equation.

$$Alkalinity = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \qquad \text{Equation 2}$$

In pure or condensed water, with or without dissolved CO_2, the alkalinity is zero. When considering more complex solutions, containing dissolved CO_2 and H_2S species, organic acids (acetic acid is the most common one with its conjugate base CH_3COO^-, expressed as Ac^-), and various dissolved salts, the expression of alkalinity becomes:

$$Alkalinity = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [Ac^-] + [HS^-] + 2[S^{2-}] - [H^+]$$

Equation 3

The alkalinity can also be expressed as a function of the dissolved salt ions, such as Na^+, Ca^{2+}, K^+, Mg^{2+}, Sr^{2+}, Cl^-, SO_4^{2-} (these are only the most commonly encountered ions in brines):

$$Alkalinity = \sum y[Anion^{y-}] - \sum x[Cation^{x+}] \qquad \text{Equation 4}$$

Although the equations shown above are relatively straightforward, getting access to the actual species concentrations from field operations is complicated. Preservation of liquid samples taken from the field is an issue and the accuracy of the measurements is often questionable. In addition, unfortunate, yet consistent, efforts to simplify the sampling and analysis procedure have led to the emergence of many misconceptions. This has contributed to a certain level of confusion in connection with the concept of alkalinity. Generally, bicarbonate is the predominant buffer for brines in the oil and gas industry since all oil wells contain carbon dioxide. The total alkalinity is assumed equal to the concentration of bicarbonate ions in brine samples. However, this relationship no longer holds in the presence of weak organic acids, often found in oil field brines, or any other weak acids (and conjugate bases) since they would also contribute to alkalinity. In practice, the alkalinity of a brine sample is determined in a laboratory using acid-base titration [17]. It is common to convert the alkalinity, initially measured in mol/L, to ppm_w HCO_3^- and express it as “equivalent bicarbonate concentration”, which can be misleading since there can be several contributors to alkalinity (Equation 3). Nevertheless, accurate titrations of brine samples collected from the field are a necessary and essential step in calculating the *in situ* pH in the reservoir and along production pipelines, since alkalinity does not change with temperature and pressure under operating conditions [18].

The value of alkalinity is a fundamental parameter in corrosion prediction software such as the Ohio University flagship model MULTICORP^{TM} [19]. The user must know either the pH of the water sample or the alkalinity while defining the composition of the water phase. Inaccurate knowledge of the alkalinity can lead to erroneous pH predictions and consequently faulty corrosion rate estimations. As mentioned earlier, the higher the alkalinity, the greater is the ability of the brine to resist changes in pH. Given a set gas composition and temperature, the brine pH will typically be the lowest if the alkalinity is zero (except possibly during acidizing, when acids are injected intentionally in the well formation to dissolve solid deposits and increase production). This scenario, which corresponds to pure or condensed water, is typically the most corrosive (at least in terms of uniform corrosion). As the alkalinity increases, pH also increases and the corrosivity of the brine decreases. An example of the importance of alkalinity is shown in Figure 1, as a range of conditions is simulated using MULTICORP^{TM}. Table 1 lists the simulation conditions, using constant values for temperature and gas compositions, but changing the alkalinity. The model results confirm that increasing the alkalinity increases pH and can decrease significantly the corrosivity, particularly if conditions favor the formation of iron carbonate scales. The simulation results, shown in Table 2, also show clearly that a misestimation of the alkalinity can have a great effect on the predicted corrosion rate and can lead to the inappropriate selection of corrosion mitigation techniques.

Table 1: *Conditions used for the prediction of pH and corrosion rates for 0.005 and 0.05 M total alkalinity using MULTICORP*^{TM}.

Modeling Conditions	
Temperature (ºC)	80
Pressure (bar)	40
Corrosion type	Bottom-of-the-line-corrosion
Flow type	Single phase water flow
Simulation	Point model
% CO_2 gas content	10
Na^+ (M)	0.86
Cl^- (M)	0.86

Table 2: *Predicted pH and corrosion rates for 0.005 and 0.05 M total alkalinity using MULTICORP*^{TM}.

Total Alkalinity (M)	Predicted pH	Corrosion Rate (mm/yr)
0.005	5.55	1.02
0.05	6.55	0.26

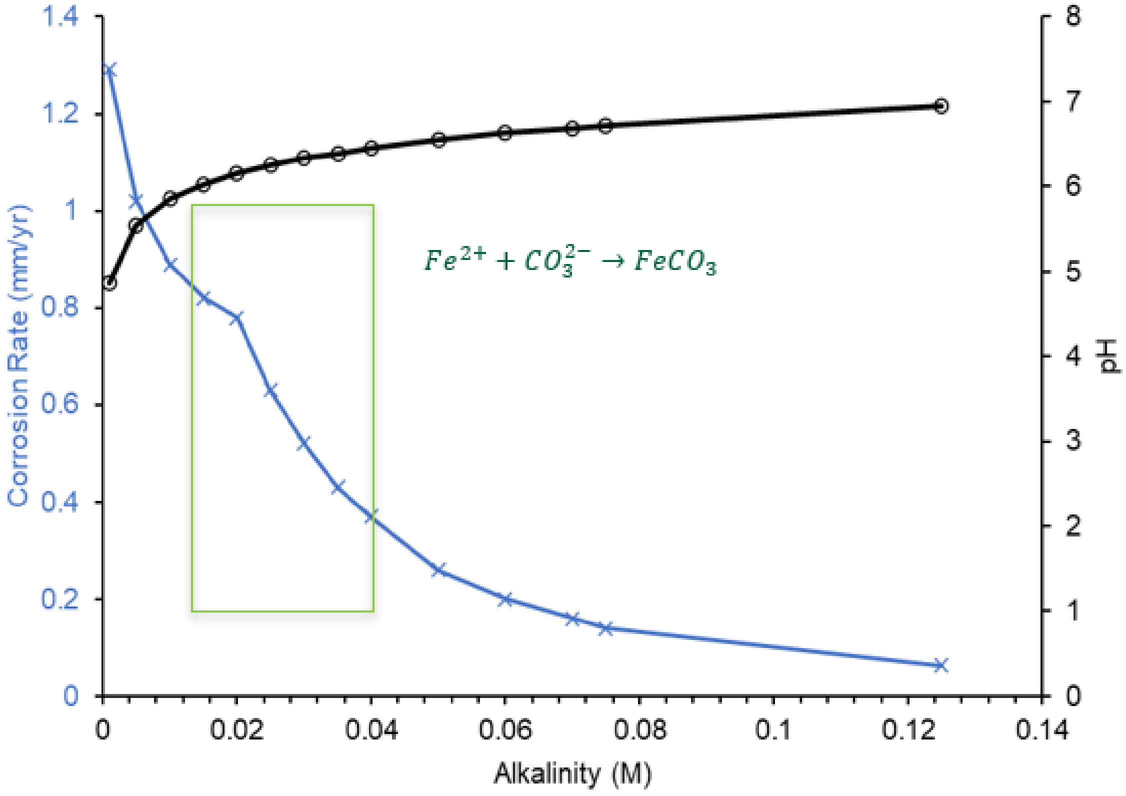


Figure 1: *Effect of alkalinity on predicted corrosion rate and pH at in situ conditions using MULTICORP*^{TM}.

2.6 Development of the Alkalinity Equation

The alkalinity equation can be broken down further by defining each of the terms on the right side of Equation 2 in terms of equilibrium constants, partial pressure CO_2 and both H_2S and H^+ concentration. The list of the main chemical reactions involved in the alkalinity equation can be found in Table 3. The calculations of each equilibrium *K* value for the dissolution and dissociation reactions are listed in Table 4.

Table 3**:** *Chemical reactions accounted for in the alkalinity equation [7]*

	Reaction	**Equilibrium Constant**
Solubility of CO_2 (M/bar)	$CO_{2\,(g)} \rightleftharpoons CO_{2\,(aq)}$	$K_{sol} = \frac{[CO_2]}{P_{CO_2}}$
CO_2 Hydration	$CO_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3\,(aq)}$	$K_{hy} = \frac{[H_2CO_3]}{[CO_2]}$
Carbonic Acid Dissociation (M)	$H_2CO_{3\,(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3\,(aq)}$	$K_{ca} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$
Bicarbonate Anion Dissociation (M)	$HCO^-_{3\,(aq)} \rightleftharpoons H^+_{(aq)} + CO^{2-}_{3\,(aq)}$	$K_{bi} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$
Water Dissociation $(M)^2$	$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$	$K_{wa} = [H^+][OH^-]$
Acetic Acid Dissociation (M)	$HAc_{(aq)} \rightleftharpoons H^+_{(aq)} + Ac^-_{(aq)}$	$K_{HAc} = \frac{[H^+][Ac^-]}{[HAc]}$
Solubility of H_2S (M/bar)	$H_2S_{(g)} \rightleftharpoons H_2S_{(aq)}$	$K_{H_2sol} = \frac{[H_2S]}{P_{H_2S}}$
H_2S Dissociation (M)	$H_2S_{(aq)} \rightleftharpoons H^+_{(aq)} + HS^-_{(aq)}$	$K_{H_2S} = \frac{[H^+][HS^-]}{[H_2S]}$
HS^- Anion Dissociation (M)	$HS^-_{(aq)} \rightleftharpoons H^+_{(aq)} + S^{2-}_{(aq)}$	$K_{HS^-} = \frac{[H^+][S^{2^-}]}{[HS^-]}$

Table 4*: List of dissociation reactions and their calculated equilibrium constants [7]*

	Equilibrium Constants
Carbonic Acid Dissociation (M)	$K_{ca} = 387.6 \times 10^{-\left(6.41-1.594\times\left(10^{-3}\right)\times \mathrm{T_f}+8.52\times\left(10^{-6}\right)\times\left(\mathrm{T_f^2}\right)-3.07\times\left(10^{-5}\right)\times \mathrm{P_{psi}}-0.4772\times\left(\mathrm{I_s^{0.5}}\right)+0.118\times \mathrm{I_s}\right)}$
Bicarbonate Anion Dissociation (M)	$K_{bi} = 10^{-\left(10.61-4.97\times\left(10^{-3}\right)\times \mathrm{T_f}+1.331\times\left(10^{-5}\right)\times\left(\mathrm{T_f^2}\right)-2.624\times\left(10^{-5}\right)\times \mathrm{P_{psi}}-1.166\times\left(\mathrm{I_s^{0.5}}\right)+0.3466\times \mathrm{I_s}\right)}$
Solubility of CO_2 (M/bar)	$K_{sol} = \left(\frac{14.5}{1.00258}\right) \times 10^{-\left(2.27+5.65\times 10^{-3}\times \mathrm{T_f}-8.06\times 10^{-6}\times\left(\mathrm{T_f^2}\right)+0.075\times \mathrm{I_s}\right)}$
Acetic Acid Dissociation (M)	$\mathrm{K_{HAc}} = 10^{-\left(6.66104-0.0134916\times \mathrm{T_k}+2.37856\times 10^{-5}\times(\mathrm{T_k})^2\right)}$
Water Dissociation $(M)^2$	$\mathrm{K_w} = 10^{-\left(29.3868-0.0737549\times \mathrm{T_k}+7.47881\times\left(10^{-5}\right)\times\left(\mathrm{T_k^2}\right)\right)}$
CO_2 Hydration (M)	$K_{hy} = 2.58 \times 10^{-3}$
Solubility of H_2S (M/bar)	$K_{H_2S_{sol}} = 10^{-0.71742627-0.012145427\times T_c+5.6659982\times 10^{-5}\times T_c^2-8.1902716\times 10^{-8}\times T_c^3}$
HS^- Anion Dissociation (M)	$K_{HS^-} = 10^{-\left(23.93-0.030446\times T_k+2.4831\times 10^{-5}\times T_k^2\right)}$
H_2S Dissociation (M)	$K_{H_2S} = 10^{-\left(15.345-0.045676\times T_k+5.9666\times 10^{-5}\times T_k^2\right)}$

Note: In Table 4, T_f is temperature in degrees Fahrenheit, T_k is absolute temperature in Kelvin, I_s is ionic strength in molar, and P_{psi} is the partial pressure of CO_2 in psi.

Considering all the equations listed above, the alkalinity equation reduces to Equation 5 [7]:

$$\mathrm{Alkalinity} = \frac{\mathrm{K_{ca}K_{hy}K_{sol}P_{CO_2}}}{[\mathrm{H^+}]} + \frac{2\mathrm{K_{bi}K_{ca}K_{hy}K_{sol}P_{CO_2}}}{[\mathrm{H^+}]^2} + \frac{\mathrm{K_{HAc}[T_{HAc}]}}{[\mathrm{H^+}]} + \frac{K_{H_2S}K_{H_2S_{sol}}P_{H_2S}}{[H^+]} + \frac{K_{HS^-}K_{H_2S}K_{H_2S_{sol}}P_{H_2S}}{[H^+]^2} + \frac{\mathrm{K_w}}{[\mathrm{H^+}]} - [\mathrm{H^+}] \qquad \text{Equation 5}$$

As mentioned earlier, accurate determination of alkalinity is essential in determining the *in situ* pH of produced brines in operating conditions. Equation 5 holds of course for field (a.k.a. production) conditions but measurement of *in situ* pH impractical inside a high pressure, high temperature oil and gas pipeline. However, Equation 5 still holds in laboratory conditions, where pH can be readily measured and where CO_2 or H_2S content, as well as temperature, can be controlled easily. Since it is a conserved variable, the alkalinity of a brine will be the same if it is measured in field and in laboratory conditions. In practice, the measurement of alkalinity of a brine sample in a laboratory is performed by acid-base titration. The liquid samples have been typically degassed and filtered prior to the titration to remove any solid precipitates. The fundamentals of acid-base titration are presented in the next chapter.

2.7 Fundamentals of Titration

An acid-base titration is a quantitative analytical method used to measure the concentration of an acid or a base in a liquid sample. When titrating a basic solution, a strong acid, with a known concentration, is typically used as the titrant. The solution of unknown concentration is referred to as the titrand. The main types of titrations include pH-based titrations and endpoint titrations including titrations with colorimetric indicators.

Endpoint titrations are used when a specific volume of titrant is being measured to reach a predetermined pH value. This is often done by adding a colorimetric indicator to the titrand solution before the titration is started. The endpoint is then identified by a change in color to the solution after a certain volume of titrant is added. Literature defines that, for titrating HCO_3^- at 25°C, a defined endpoint of 4.5 pH should be used per ASTM 1067D [20][21][22].

Inflection point titrations make use of direct pH measurements instead of colorimetric indicators. An acid solution of know concentration (titrant) is added in small increments to the tested brine and the pH of the solution is recorded. The shape of the pH vs. added titrant volume is then used to determine the alkalinity of the solution.

The ASTM 1067D standard indicates that inflection point titrations provide a more accurate analysis of sample composition, but result in process control errors. However, endpoint titrations have the potential for much greater errors in the determination of alkalinity, especially if the solution contains weak bases other than HCO_3^-, invalidating the defined endpoint of 4.5 pH. Yet, the standard recommends using an endpoint type titration due to practical considerations – it is a much easier, cheaper and faster method than an inflection point titration and it produces a very simple output. However, it does not provide any indication about the validity of the measurement and can yield wrong results.

The inflection point titrations, for which known volumes of titrant are added, in small increments, to the brine and for which the pH of the solution is recorded, do not often display a very clearly defined endpoint. Yet; it only reflects the complexity of a given brine composition – complexity that could never be captured by an endpoint titration. The shape of the titration curve (pH *vs.* added titrant volume) can be analyzed to determine the total alkalinity of the solution from the equivalence point at the maximum value of d(pH)/d(ml) [23]. This term “d(pH)/d(ml)”, often used in titration terminology, is the derivative of “pH *vs.* added titrant volume”, a.k.a. the slope of the measured pH *vs.* titrant volume curve (the notation “ml” stands for the titrant volume in milliliters). This volume of titrant can be converted to molar alkalinity based on the concentration of acid used and displayed as d(pH)/d(C). This method can be used to recalculate the *in situ* pH in operating conditions, as long as other information (operating pressure and temperature, partial pressure of CO_2, total organic acid concentrations) is also known. An example of a titration curve conducted on deionized water containing 0.1 M $NaHCO_3$ can be seen in Figure 2. The pK_a referred to as the midpoint of titration is located at 6.4 pH where the concentrations of H_2CO_3 and HCO_3^- are equal, found in Equation 7. The equivalence point, which corresponds to the point where the curve tends to become vertical (the chemical reaction between H^+ and HCO_3^- ends), is also quite clear. Equivalence points are not defined at a specific pH value and are determined from titration data and located at the maximum d(pH)/d(C), this allows them to have higher accuracy and better represent the presence of weak bases. An endpoint of titration refers to a predetermined stopping point at a specified pH, as defined as pH 4.5 sacrificing the accuracy of analysis for ease of sampling.

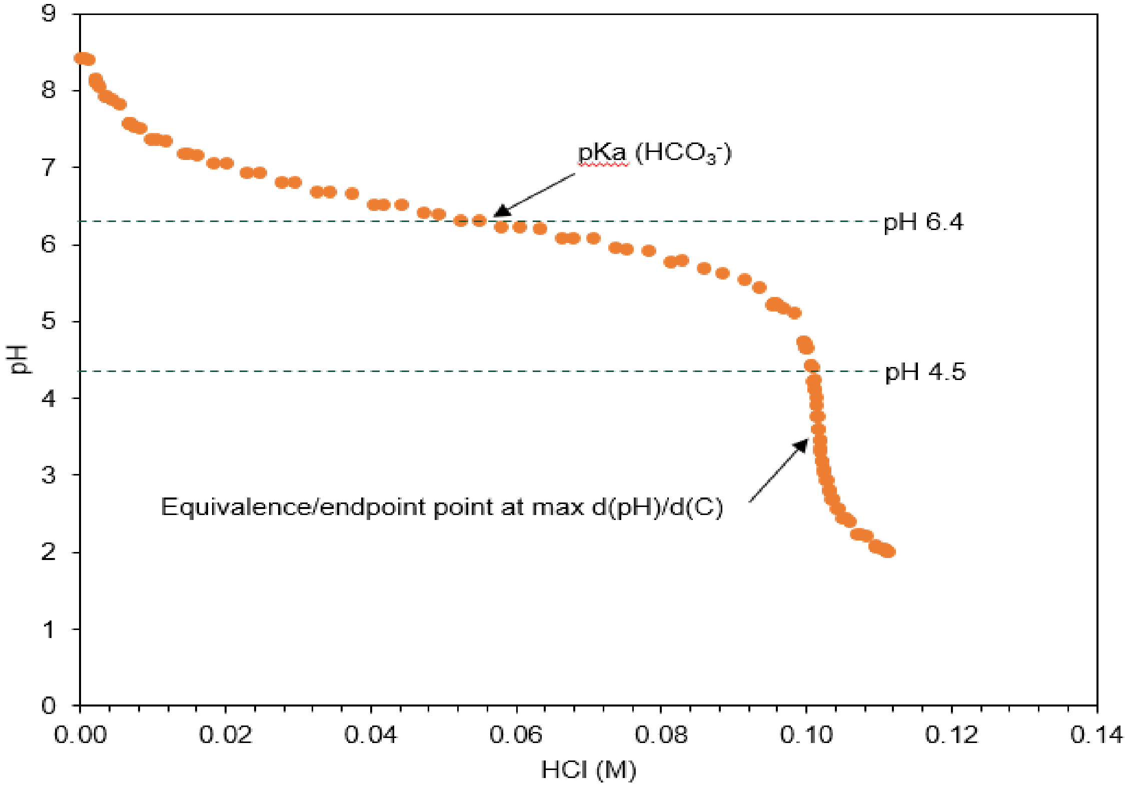


Figure 2: *Titration curve of a 100 ml sample containing 0.1 M* $NaHCO_3$ *with 1.0 M HCl.*

Titrations between a strong acid (*i.e.*, HCl) and a strong base (*i.e.*, NaOH) have a very defined equivalence point at a neutral pH of 7, as is shown in Figure 3. The full dissociation of all ions in solution when strong acids and bases are added together give the titration curve this characteristic. Organic acids and bicarbonate species do not dissociate fully in solution; therefore, they are defined as weak bases. Strong acid - weak base titration curves display much shallower (less vertical) inflection points. Shallower inflection points can be harder to detect and less noticeable on a pH *vs* Volume of titrant graph. The reaction of bicarbonate ion, reverse of Reaction 6, and acetate ion, reverse of Reaction 8, are both examples of strong acid - weak base reactions; both take place in titration of produced water samples. The addition of HCl increases the concentration of H^+ driving the reactions to the left, consuming the HCO_3^- and CH_3COO^- species.

When titrating the acid into the base for a strong acid-weak base titration, the pH of the analyte will start high and drop gradually with the addition of acid until the measurements conclude after a rapid pH transition signifying the equivalence point [23][24][25]. The volume of known concentration of acid is then used to determine the molar concentration of the base in the analyte. Figure 3 below shows examples of a strong acid - weak base titration curve compared to strong acid strong base titration data.

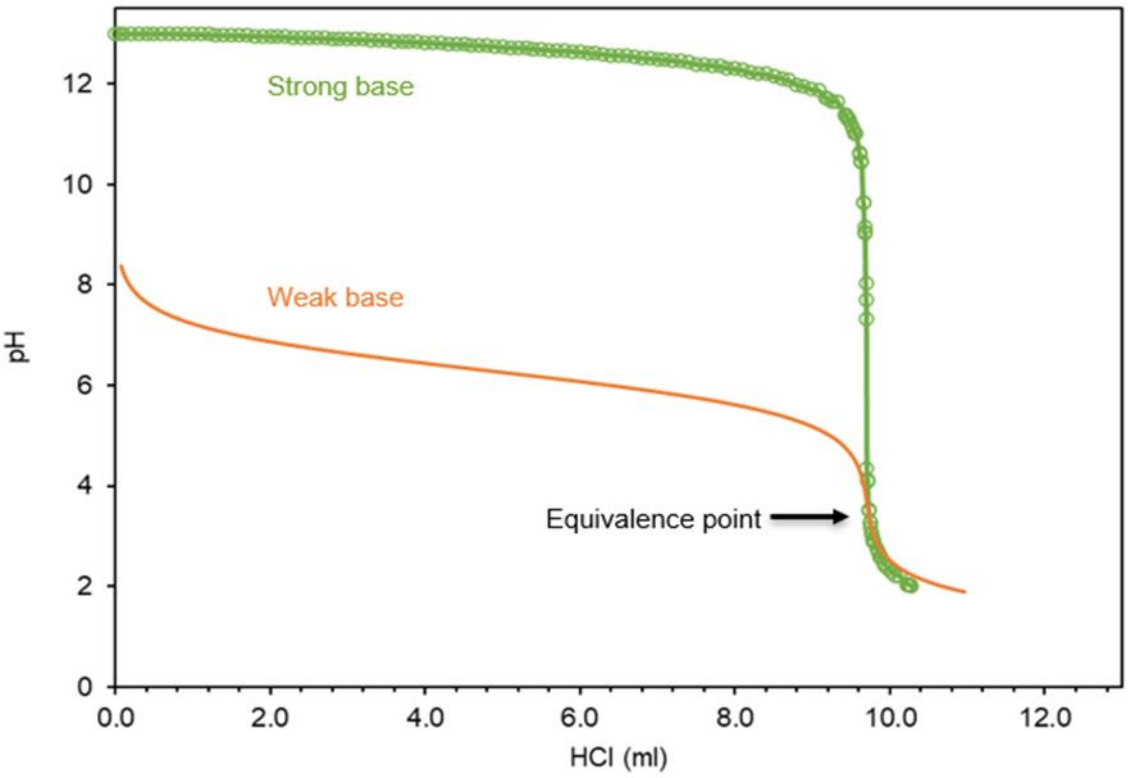


Figure 3: *Comparison of titrations carried out on strong and weak bases using a 1 M HCl solution as the titrant.*

2.8 Rice Titration Methodology and Model

The Rice method is an experimental procedure that can be used to determine the total alkalinity and the concentration of carboxylate salts (i.e. organic acid) from unknown produced oilfield brine samples. The method was proposed and published by Rice University as a deliverable of a Brine Chemistry Consortium group [26]. The information about the Rice method and the programs that go along with it are proprietary to the consortium's sponsors. However, key aspects of the methodology have been shared in the scientific literature. The methodology to measure alkalinity from preserved brine samples is as follows [26]:

- The sample is collected and preserved by dilution, acidification, or stored under CO_2. Then after arriving at the lab the sample is filtered to remove solid precipitates present in the sample that would otherwise interfere with titration results. The solid precipitates in solution originate from insoluble iron and calcium salts under atmospheric conditions.
- The mass of precipitated iron and calcium salts on the filter is then extracted with 1 N HCl and analyzed by ICP (induction coupled plasma spectroscopy) to be added back later after titration. Precipitates of iron and calcium salts react with the same species which contribute to alkalinity in the form of $Fe(OH)_3$, $FeCO_3$, and $CaCO_3$ precipitation creating a source of error.
- The brine sample is equilibrated with 1% $CO_{2(g)}$ and balance $N_{2(g)}$ at 25ºC using a constant sparge during and before titration in the titration vessel, CO_2 equilibrium is established before titration after 30 minutes of sparging.

- The brine sample is titrated using 10-15 data points from the initial to the final pH of 3. The time between titrant additions was not available in the rice publications, times between titrant additions were therefore tested.
- The Rice equation (Equation 6) is fitted to the titration data using a nonlinear least square curve-fitting routine. The values of Alk, TAc^-, $fHCO_3^-$, and fAc^- are adjusted to obtain the best fit of the experimental data.

$$HCl(M, calc) = Alk + \frac{10^{-pH}}{\gamma^{H+}} - \left[\frac{fHCO_3 * K_{1,H_2CO_3} * K_{CO_2} * P_{CO_2,gas} * \gamma_{g\,CO_2}}{10^{-pH} * \gamma_{HCO_3^-}} + \frac{TAc^-}{\frac{10^{-pH} * \gamma_{Ac^-}}{fAc * K_{HAc} * \gamma_{HAc,eq}} + 1} + \frac{K_w}{10^{-pH} * \gamma_{OH^-}}\right]$$

Equation 6

Table 5: *Table of variables used in the Rice Equation.*

Alk	Total Alkalinity (M)
TAc^-	Sum of carboxylate species (M)
P_{CO_2}	CO_2 Partial Pressure (bar)
K	Equilibrium Constants
γ	Activity Coefficients
$fHCO_3^-$, fAc^-	Correction Factor for "true" activity coefficients ≈ 1

- The total alkalinity (mg/L) is then calculated by adding the alkalinity value from titration of the filtered brine with the concentrations of iron and calcium that formed precipitates. This is done by multiplying by the molecular weight ratios of 2 moles of HCO_3^- *vs* 1 mole iron or calcium, conversion factors of 2.18 and 3.05 respectively as shown in Equation 7 [26].

$$Alkalinity\left(\frac{mg}{L}\right) = ALK_{titration}\left(\frac{mg}{L}\right) + \frac{2[HCO_3^-]}{[Fe^{2+}]}\left(\frac{mg}{L}\right) + \frac{2[HCO_3^-]}{[Ca^{2+}]}(\frac{mg}{L})$$

Equation 7

The titration procedure indicates that the brine is titrated at room temperature after a 30-minute CO_2 sparge to establish an equilibrium with a set partial pressure of CO_2. The sparge also sets the initial pH in the sample to the equilibrium value corresponding to the partial pressure of the CO_2 sparge gas. The CO_2 sparge is not actually necessary to determine the total alkalinity, as this variable is conserved and does not depend on the presence of gaseous CO_2. However, it helps to highlight the contribution of HCO_3^- and carboxylate ions (conjugate base of organic acid) in the titration curve and make the analysis easier. Decreasing the partial pressure of CO_2, which in turn increases the initial pH, highlights the alkalinity contribution of HCO_3^- and organic acid.

As mentioned earlier, the data collected using small additions of titrant under constant sparge can be fitted using the Rice equation. Water samples are titrated in small increments as small as 2 ml/hr allowing the pH to re-establish equilibrium after each acid addition under active sparge. Titration of the sample is done from the original pH to a final pH of 3 [26]. The Rice equation (Equation 6) is fitted to the data collected from titration in using a non-linear least square curve-fitting routine. The values of Alk, TAc^-, $fHCO_3^-$, and fAc^- are changed to obtain the best fit of the data.

According to Mason Tomson's SPE 93266 publications [26], one of the main purposes of the Rice method is to help identify if organic acids are present in the brine sample. The presence of organic acid is not always checked in routine water analysis, but this omission can lead to severe misinterpretation of the total alkalinity present in a specimen. In their experimental work, the authors applied their titration method to brines containing different concentrations of carboxylates (with ionic strengths ranging from

0.3– 2.5 M) and then fitted their prediction with the experimental data by adjusting the value of TAc^{-} in the Rice equation. The R^2 value derived from the comparison between the known concentration and the curve fitted values was 0.9946, thus validating the methodology.

The Rice equation originates from the electroneutrality equation but omits the effect of H_2S (assuming no H_2S is present) and the dissociation of HCO_3^{-} (which contribution is negligible in the range of pH tested). In addition, it takes into account the non-ideality of the solution by the use of activity coefficients and correcting factors. When dealing with brines with low salt content (ionic strength below 0.5 M), these activity coefficients and correcting factors are all taken as unity. For higher salt content brines, the activity coefficients can be obtained through applicable models (Debye–Hückel theory, Pitzer theory, or OLI's MSE model) and the correction factors are adjusted to obtain a better fit.

Rice University has created their own proprietary program, "Rice BCC Alk-TAc at PCO2.xls" [27] that fits the experimental titration curve with Equation 6 by minimizing the sum of the squares of the residuals. The non-linear regression (using Newton-Raphson procedure in Excel Solver®) is made by changing the values of Alk, T_{Ac}, f_{Ac} and f_{HCO3-} [28][29]. An example of a predicted titration curve generated using a derived form of Equation 6 is shown in Figure 4, considering an aqueous solution containing HCO_3^{-} and CH_3COO^{-}. The first inflection point represents the point where all HCO_3^{-} has been consumed. The remaining alkalinity in solution exists in the form of CH_3COO^{-}. The second inflection point represents the consumption of the remainder of the solution alkalinity. The location of the equivalence point labeled in Figure 4 is represented by the maximum value of the d(pH)/d(C) along with the value of total alkalinity. The Rice Equation output data is plotted with titration data collected in the ICMT laboratory (considering a relatively simple aqueous solution containing the corresponding concentrations of bicarbonate and acetate ions). The experimental titration data collected in Figure 4 was carried out on a 100 ml mixture of 0.1 M HCO_3^-, 8.5 mM total CH_3COO^- at 27°C and 0.01 bar pCO_2 (1% CO_2). The equation does allow for an accurate approximation of the total alkalinity to be made with less than 1% error at the equivalence point between the collected data and the modeled curve.

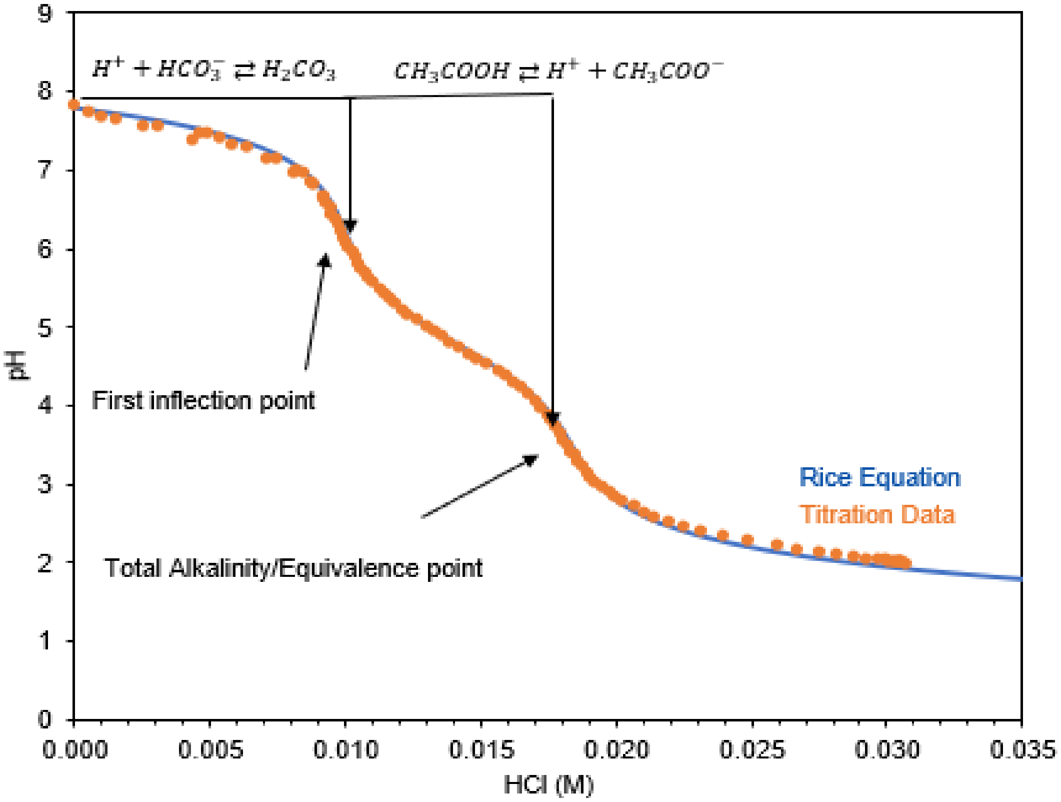


Figure 4: *Rice titration curve generated from Equation 6 and compared to titration data from a known brine (100 ml): 0.01 M* $NaHCO_3$ *and 0.0085 M* CH_3COONa*, 0.01 bar* P_{CO2}*.*

The modeled d(pH)/d(C) from the Rice equation from Figure 4 can be seen in Figure 5 with the highlighted peaks. The steepest part of the curve provides the maximum d(pH)/d(C) where the largest rate of change occurs. When plotted as d(pH)/d(C) *vs.* molar concentration of titrant, the peaks provide the contribution of bicarbonate (first inflection point) and organic acid concentration (equivalence point). The example above has the first inflection point located after 10 ml of 1 M HCl was added to the 100 ml sample, representing a concentration of HCO_3^- of 0.1 M. The organic acid contributes to the value of alkalinity past the first equivalence point and continues to the second equivalence point maximum d(pH)/d(C). The alkalinity contribution from CH_3COO^- is determined by the difference between the first inflection point and the equivalence point at the maximum d(pH)/d(C). No fitting exercise was performed to match the Rice Equation with the experimental data since the solution composition was known, and since the salt content is low (*i.e.* solution is near ideal). Instead, the actual values of the bicarbonate and acetate ions were used directly.

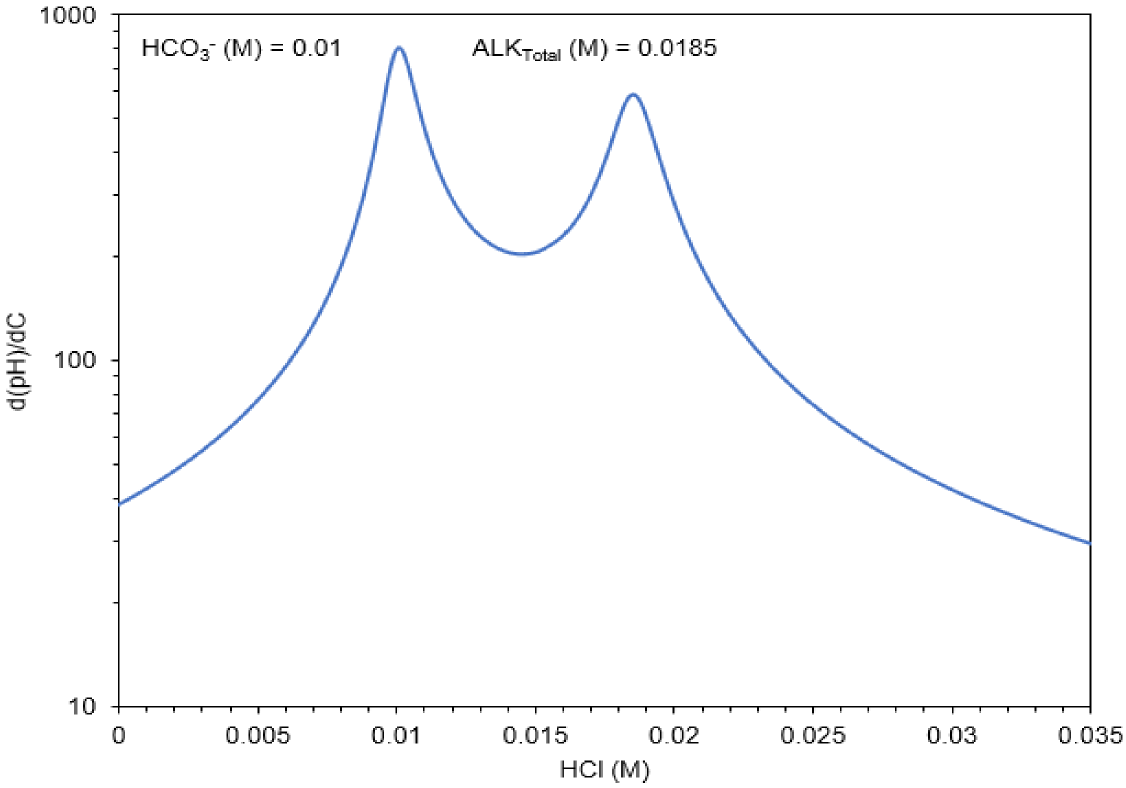


Figure 5: *Rice titration curve modeled with d(pH)/d(C) fit to titration data from a known brine (100 ml): 0.01 M* $NaHCO_3^-$ *and 0.0085 M* CH_3COOH.

The Rice equation is just one way to model titration data collected in the laboratory. It is meant to fit experimental titration data obtained with a CO_2 gas sparge. The requirement of equilibrium between the carbonic species in the liquid and the gaseous CO_2 involves additional time and resources. The fundamental methodology for performing typical acid/base titration does not require CO_2 sparge. The typical method is easier to complete but also comes with some drawbacks, when applied to systems containing bicarbonate and carboxylate ions. This methodology is referred in this document as the Henderson methodology.

2.9 Henderson-Hasselbalch Titration Methodology and Model

Typical titrations are often performed at atmospheric conditions, where pCO_2 is approximately equal to 0.04 mol%, and do not involve a sparge or additional equipment. More importantly, since there is no gas sparge, there is no condition of equilibrium between the carbonic species in solution and the atmospheric CO_2. This type of titrations is referred, in this document, as following the Henderson methodology. It is designed to be used with samples containing a specific concentration of a undissociated weak acid(s) $[HA_{free}]$ (total carboxylate species), along with its conjugate base(s) $[A^-]$; in combination referred to as buffers. The pH of buffer solutions can be described using the Henderson-Hasselbalch equation, see Equation 8 below.

$$pH = pK_a + log\frac{[A^-]}{[HA]} \qquad \text{Equation 8}$$

A generic weak acid-base dissociation reaction is written in Reaction 9.

$$HA_{free} \leftrightharpoons A^- + H^+ \qquad \text{Reaction 9}$$

Experimental data obtained through the Henderson methodology can be modeled. The modeled titration equation is referred to, for consistency, as the Henderson Equation. This equation is derived, as the Rice equation, from the electroneutrality equation. It differs from the Rice equation on how it treats the bicarbonate concentration term (*i.e.* whether or not equilibrium with the CO_2 sparge is considered). The Henderson equation is expressed, in terms of pH *vs* concentration of titrant, in Equation 9. The terms T_{HCO3-} and T_{Ac-} are total molar concentrations of bicarbonate (as $NaHCO_3$) and acetate (as CH_3COONa) added, respectively. Other species of organic acid can be added to the Henderson equation by adding an additional term of the same form. The derivation from the electroneutrality equation to the Equation 9 can be found in the appendix. Equilibrium constants for the carbonic acid dissociation (K_{ca}) and acetic acid dissociation (K_{HAc}) for the reactions can be found in Table 4.

$$HCl(M, calc) = 10^{-pH} + \frac{T_{HCO3-}}{\frac{K_{ca}}{10^{-pH}} + 1} + \frac{T_{Ac-}}{\frac{K_{HAc}}{10^{-pH}} + 1} \qquad \text{Equation 9}$$

The Henderson equation can model the behavior of the titration curve over the entire pH range. The Henderson equation can include the contributions of any bicarbonate or carboxylate salts to the total alkalinity. As an example, Equation 9 lists the contribution to alkalinity by bicarbonate and acetate ions, respectfully, where T_{HCO3-} and T_{Ac-} are total species concentrations (M). The equilibrium constants for these reactions, K_{ca} and K_{Hac}, are expressed in (M). Titration data from a sample containing both bicarbonate and organic acid is modeled using Equation 9 below in Figure 6. The Henderson equation works well for modeling titration data collected at atmospheric conditions, without gas sparging, with bicarbonate and organic acids present in the sample.

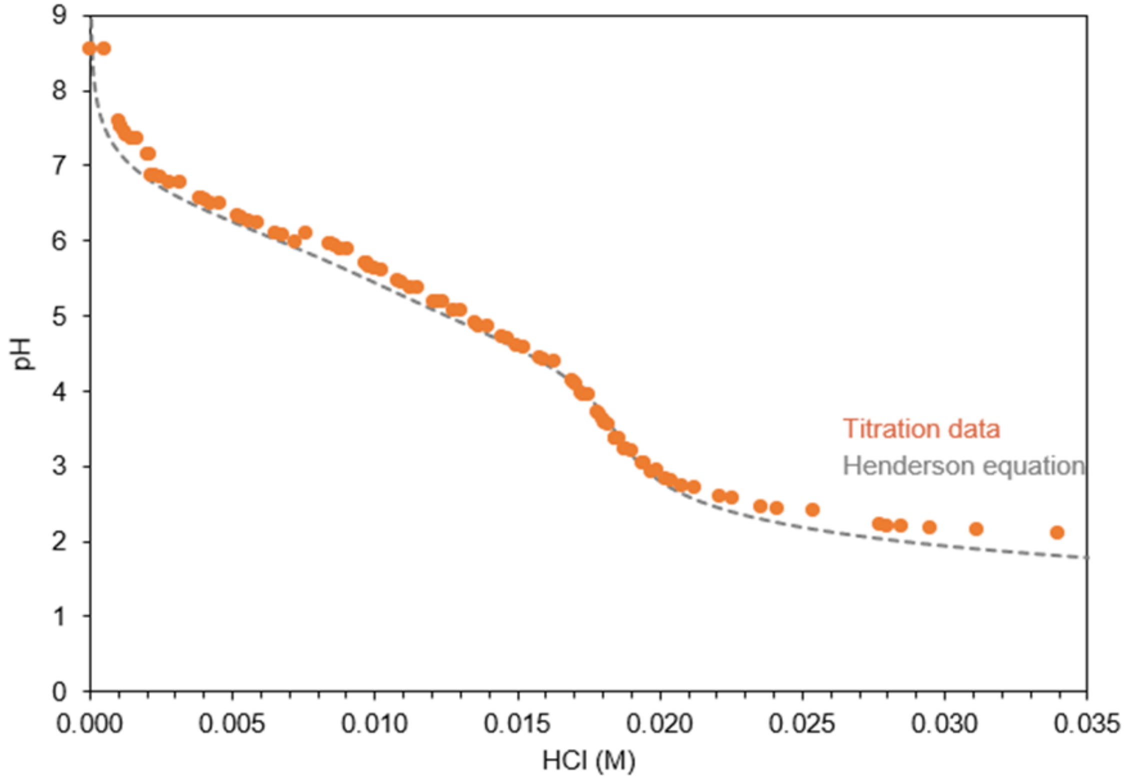


Figure 6: *Titration of an aqueous sample modeled to the Henderson equation (Equation 9) containing 0.01 M* $NaHCO_3$*, and* CH_3COONa *0.0085 M.*

The Henderson and Rice equations can both be used to model titration data collected from field brine analysis. The Henderson equation is used throughout academia while the Rice equation is used primarily in the oil and gas industry. The Henderson equation is used for modeling titration curves collected from samples with known chemical species since no sparge is used to set equilibrium conditions. The Rice equation is used for alkalinity determination of samples with unknown composition at fixed CO_2 partial pressure. As stated above, the main difference between the Rice and Henderson equations is how the $[HCO_3^-]$ term is treated.

$$[A^-] = \frac{[HA_T]}{10^{pka-pH} + 1}$$ Equation 10

Equation 11

$$[HA] = \frac{[HA_T]}{10^{pH-pka} + 1}$$

The experimental data collected in Figure 7 is representative of a titration curve collected without a CO_2 sparge, thus not strictly following the Rice method. The collected titration data is representative of a more standard weak base titration that typically does not require gas sparging and aligns with the Henderson equation method [23] [30]. While the Rice equation can accurately predict the inflection points corresponding to the contributions to alkalinity of both ions, large deviations for the experimental data are clear at higher pH, if the sample is not held at equilibrium with a set partial pressure of CO_2 (0.01 bar in the case of the modeled Rice equation). With CO_2 sparge, the starting pH is naturally lower and the buffering effect is stronger (*i.e.* smaller changes in pH are measured when the titrant is added). As mentioned earlier, the presence of gaseous CO_2 does not change the value of the total alkalinity, however, it changes the shape of the curve and makes the contribution of carboxylates to the total alkalinity more pronounced.

When plotting the titration data as d(pH)/d(C) *vs.* molar concentration of titrant, as shown in Figure 8, only one equivalence point is clearly visible at the total alkalinity when considering the Henderson equation. The first equivalence point is not as pronounced as when CO_2 sparge is used. The use of a CO_2 sparge only aids in separating the contributions of $NaHCO_3$ and CH_3COONa to the total alkalinity.

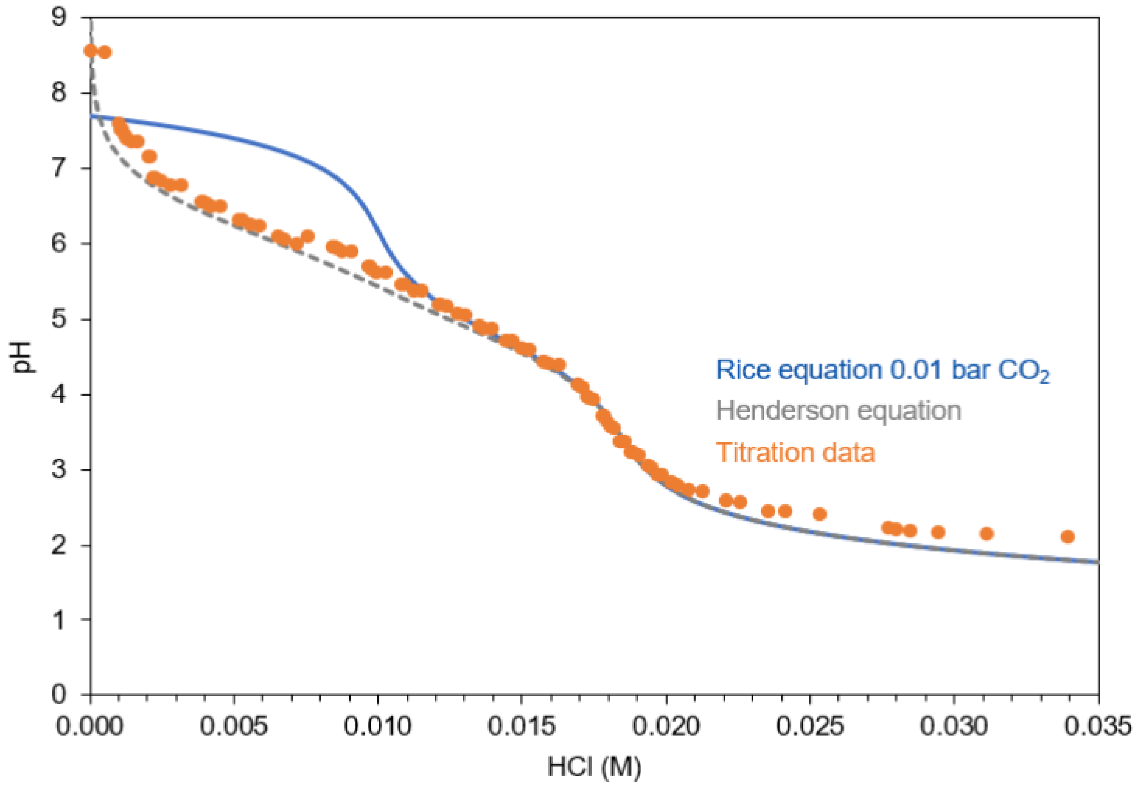


Figure 7: *Rice and Henderson titration curves compared to titration data without 0.01 bar* CO_2 *sparge from a known brine (100 ml): 0.01 M* $NaHCO_3$ *and 0.0085 M* CH_3COONa*.*

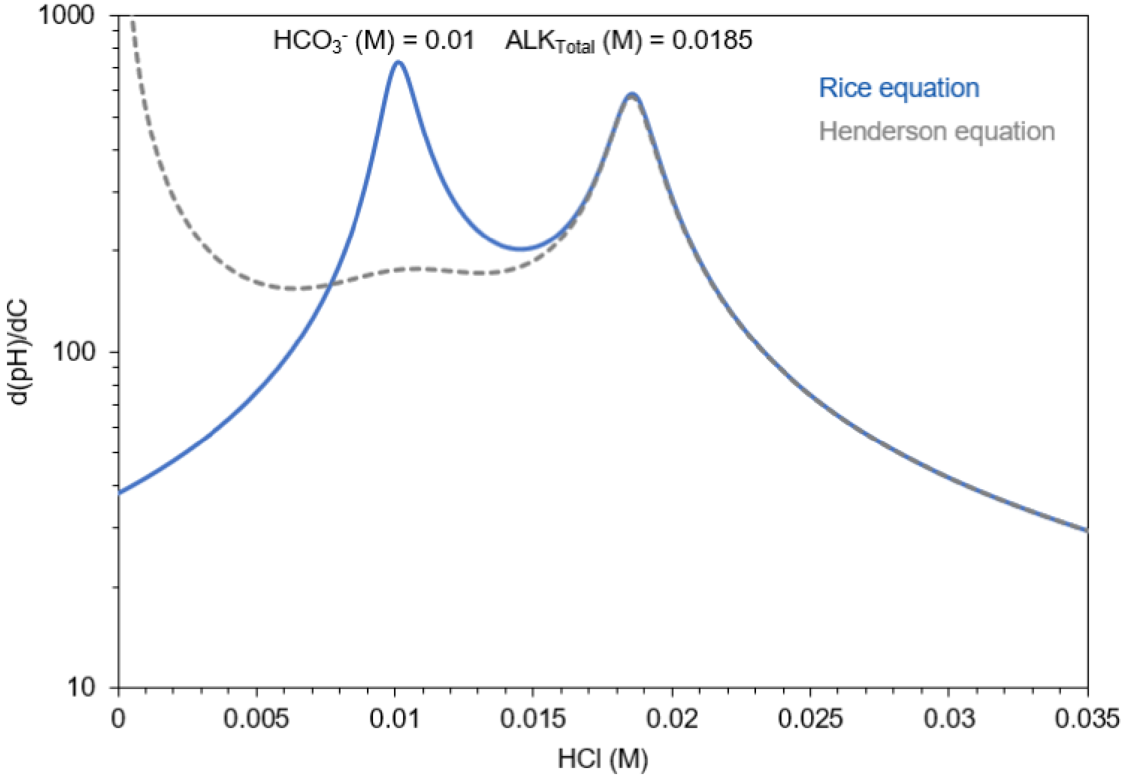


Figure 8: *Rice and Henderson titration data collected with/without 0.01 bar CO_2 sparge modeled with d(pH)/d(C) from Figure 7 a known brine (100 ml): 0.01 M $NaHCO_3^-$ and 0.0085 M CH_3COONa.*

2.10 Challenges Associated with Industry Water Chemistry Analysis

The information surrounding brine speciation is a key aspect of assessing the risk of corrosion and scale formation in oil and gas pipeline systems. Brine samples are routinely taken for analysis, however, there is no standard method for how the information is reported. Important information is often left off the document - especially the method used for titration – and the reported data are consequently open for mis-interpretation. Measurements of organic acids concentration is still not standard procedure in water chemistry analysis documents. Field water chemistry analysis typically includes the concentration of many dissolved salt species (obtained through the inductively coupled plasma method), with the most common ones being Na^+, Ca^{2+}, and Cl^-. pH is also usually reported but it is often not specified if it is measured *in situ* (at operating conditions) or in a laboratory environment. In addition, no information about the temperature at which the measurement is taken or if the sample was sparged is typically provided. Finally, and most importantly, when it comes to alkalinity, large discrepancies exist on how it is measured, reported, and even on how it should be interpreted. A few examples of water chemistry analysis provided by five different chemical companies can be seen in Table 6.

Table 6: *Summary of information taken from water chemistry documentation provided by five companies.*

	Company				
	1	2	3	4	5
Field Data (T&P)					
Downhole Temp ℃			157	250	180
Downhole Pressure (psig)			1,600	100	1,500
Lab/sample port Temp ℃			138	80	70
Lab/sample port Pressure (psig)			175	15	80
pH	5.96 @23℃	8.2 @25℃	6.4	6.4	7.2
Cations (ppm)					
Na^+	56,200	18,000	23,535	27,318	35,469
K^+	833	180	328	379	422
Mg^{2+}	3,060	58	344	422	731
Ca^{2+}	13,400	430	3,239	2,369	2,813
Ba^{2+}	16.4	23	11.7	2	0.7
$Fe_{(dissolved)}$	0.38	8	244	117.3	2.85
Sr^{2+}	1,240	68	625	439	324
Al^{3+}		2	0.27		
Pb^{2+}		5	0.02		0.01
Si^{4+}		36	107.4		
B^{3+}		57	59.13		
Li^+		1.7	20.47		18
Cu^+		0.5			
Mn^{2+}		1	2.39	4.4	0.7
Anions (ppm)					
Cl^-	127,000	26,000	43,900	49,460	61,300
Br^-	630	36			
SO_4^{2-}		280	97	622	1250
BO_3^{3-}				165	
Organic Acids (ppm)					
Acetic		820			
Propionic		110			
Isobutyric		10			
Isovaleric		10			
Valeric		10			
Aqueous Gas (ppm)					
CO_2			693	400	340
H_2S			2	70	17.1
Alkalinity (ppm)					
$CaCO_3$	52	840			
HCO_3^-	32		311	219	390
Inorganic carbon		210			
Total Dissolved Solids (ppm)					
Reported	200,495	46,000		81,355	102,712
Cation-Anion Balance	-0.12	74.02	0.04	-0.05	0.00

As the table shows, there is no consistency on the way alkalinity, pH and organic acids are reported. The temperature and pressure at sampling locations is not always given when pH is reported. While it can be assumed that pH is measured at 25℃ and 1 bar pressure, it is not always true – consequently, reported pH values are often entirely ignored by operators.

Brines also contain high concentrations of dissolved salts, primarily NaCl. The sodium and chloride ions make up greater than 95% of total dissolved solids and can vary in concentration. A balance of molar cation and anion concentrations should yield no net charge. Table 6 indicates that the electroneutrality requirement is not met in four out of five brine analyses, highlighting the level of inaccuracy inherent to this type of analysis. As mentioned earlier, alkalinity can also be determined by doing the balance between dissolved salt cations and anions in Equation 4. However, there is too much uncertainty on the measurement of the most common dissolved salts for this approach to be of any use. As an example, cation/anion balances of data set four would correspond to total alkalinity value of over 3000 ppm_w HCO_3^-, while only 219 ppm_w HCO_3^- was reported. In practice, the alkalinity reported in water chemistry analysis seldomly matches the alkalinity calculated by the charge balance on the salt species [31][32].

In addition, some reports contain full listing of organic acid contents while some do not. Yet, this information is of crucial importance for corrosion and scale formation predictions.

The alkalinity is reported differently depending which company performs the analysis: ppm_w HCO_3^-, ppm_w $CaCO_3$, inorganic carbon or simply, alkalinity. Yet, bicarbonate is the most commonly used term to represent alkalinity in CO_2 systems since it is the weak base that is present in all produced water samples from oil and gas systems. However, expressing alkalinity as equivalent ppm_w HCO_3^- is by itself a simplification since several conjugate bases present in the brine are involved in the titration reactions (OH^-, HCO_3^-, CH_3COO^- etc.).

This terminology (*i.e.* associating HCO_3^- with total alkalinity) would not constitute a major issue if the titration methodology was systematically reported - yet this crucial piece of information is almost always missing. For example, only one company reported that the ASTM 1067D standard was used for performing titrations – the endpoint method to pH 4.5 was performed using a color indicator at atmospheric conditions. Knowing if the ASTM 1067D standard was followed represents a useful information by itself, even though using an endpoint pH of 4.5 can yield severe underestimation of the true alkalinity, especially in the presence of organic acid [33]. As mentioned earlier, while this approach would work considering simple aqueous CO_2 systems, it is invalid when considering complex brines and especially brines containing organic acids. In the latter case, endpoint pH of 3 or even pH 2 should be considered [23].

In summary, data reported in water chemistry analysis are notoriously inaccurate and routinely generate misunderstandings and lead to erroneous conclusions. Yet, this data is often the only source of information that operators have to characterize the corrosivity of produced water. While it may be presumptuous to recommend changes in reporting or methodologies used for field operation, a great deal of improvement can still be made by bringing clarity in the terminology currently used. Additional practical tools can also be provided to help operators on their understanding of water chemistry data and on the use of this knowledge for corrosion predictions.

Chapter 3: Objectives and Hypothesis

3.1 Objectives

The objective of this study is to develop methodologies to analyze field brine chemistry data, and to identify and extract information relevant to corrosion assessment and modeling. The work includes guidelines on how to interpret field brine chemistry data, review of methodology currently used throughout the industry, and updated methods to conduct titrations of brines over a wide range of organic acid, bicarbonate ion and salt concentrations. Water chemistry analyses from field data are reviewed and efforts are made to adapt standard data collection and methodologies for practical use by corrosion engineers in the industry.

3.2 Hypotheses

Research gaps that were identified are the lack of consistency in the industry in the way brine speciation, alkalinity, and pH are reported in water chemistry analysis of oil and gas field brines. Terminology can be confusing and easily misinterpreted. In addition, titration methodologies used to analyze water chemistry data are often not disclosed clearly. Instead, inconsistent methods, often relying on fixed equivalence points that yield little connection to actual brine composition, are commonly used.

The following hypotheses, which guided this work, are listed below:

Hypothesis 1- When conducting titrations with unknown composition, an endpoint titration at pH 4.5 should not be used to represent the true equivalence point in the sample. If brine samples are properly titrated from their original pH to a final pH of 2.0, then the equivalence point and alkalinity can be accurately determined.

Hypothesis 2- Titration curves of solutions with weak organic acids can be properly modelled over the entire pH range. The effect of organic acids can also be properly accounted for using the Rice or Henderson-Hasselbalch equations.

Hypothesis 3- The presence of high salt and/or organic acid content will tend to flatten the titration curve and make the visual interpretation of the results difficult, with no clear equivalence point. This behavior can be properly modelled with the implementation of an appropriate activity model.

Chapter 4: Scope of Work and Test Matrix

The research work is associated with water chemistry as it applies to oil field brines. Consequently, the conditions being considered in this work are CO_2/N_2 sparged environments at 25°C and 1 atm pressure. The titrations conducted are done using a potentiometric titrator to streamline experimental work. Experimental conditions involving dissolved carbonic species, organic acids, and primary salts are considered.

Table 7: *Experimental test matrix*

Test series	Set 1	Set 2	Set 3	Set 4
Investigating	**Bicarbonate**	**Carboxylate**	**Bicarbonate/Salt**	**mixed**
Species of interest	HCO_3^-	CH_3COO^-, $HCOO^-$, $CH_3CH_2COO^-$	NaCl, KCl, $MgCl_2$	HCO_3^-, 3 carboxylates, salt
Range of concentration	0.005-0.1 M	1.7-17 mM	0.005-0.1 M bicarbonate 0.1-2 M salt	0.005-0.1 M bicarbonate 1.7-17 mM acid
Ionic strength	Low (0.005-0.1)	Low (1.7-17 mM)	0.1-2 M	0.1-2 M
Measurement techniques/ variables	d(pH)/d(ml) pH vs ml (HCl)	d(pH)/d(ml), Rice Method, pH vs ml (HCl)	d(pH)/d(ml), Rice Method, pH vs ml (HCl)	d(pH)/d(ml), Rice Method, pH vs ml (HCl)

4.1 Titrations Involving Dissolved Carbonic Species

Titrations involving CO_3^{2-}, HCO_3^-, and H_2CO_3 species are performed to acquire familiarity with the experimental method and to develop baseline curves. Titrations (Table 7 #1) involving HCO_3^- concentrations (from dissolved $NaHCO_3$) from 0.005 to 0.1 M were conducted following the Rice methodology. This range of concentrations reflects literature data, as applied to the oil and gas industry, and are used as baseline conditions for the rest of the study.

4.2 Titrations Involving Organic Acid

Solutions including organic acids/carboxylates commonly found in oilfield brines are studied to characterize the corresponding endpoints of titrations. Titrations are performed using the Rice methodology. Organic acids are also referred to as carboxylates because they contain $RCOO^-$ as their functional group. Carboxylates that are studied include acetate, propionate, and formate with concentrations ranging from 0.0017-0.017 M in solution. One of the goals of this section is to investigate if the endpoint corresponding to the different carboxylates can be distinguished between themselves. Conditions from titrations (Table 7 #2) involving carboxylates are also modeled with the Rice equation.

4.3 Effects of Primary Salts

A parametric study is conducted on the effect of ionic strength and salt composition on the measurement of alkalinity (Table 7 #3), again following the Rice methodology. Salt species that make up the majority of brine samples in industry are NaCl, KCl, and $MgCl_2$. These salts are studied by varying the ionic strengths from 0.01 – 2 M. The main goal is to determine if salt is a determining factor in alkalinity or if deviations can be expected due to high ionic strength. The ionic strength of solutions containing salts are accounted for by implementing activity coefficients into the Rice equation to improve titration modeling. Activity based water speciation models are chosen for readily available models.

4.4 Mixed Species Titrations

Titrations with mixed (a.k.a. involving bicarbonate and carboxylates) species are performed using the Rice methodology (Table 7 #4). One of the goals of this section is to investigate if the endpoint corresponding to bicarbonate can be distinguished from the one(s) associated with carboxylate(s). Different compositions involving both salts and organic acids are investigated and potential synergistic effects (development of complexes for example) are reported. The intended outcome is to characterize the influence of both salts and organic acids on the shape of the titration curve generated with a known concentration of HCO_3^-.

Chapter 5: Experimental Procedure and Testing Equipment

5.1 Equipment

The test apparatus consists of a potentiometric titrator with a stirrer and connected to a general laboratory (HI1131B) glass-bodied combination pH electrode positioned above the sample. A burette is filled with 1 M HCl solution (titrant) and the liquid sample to be titrated (titrand) is placed in a 150 ml beaker that contains a stir bar. The potentiometric titrator and set up can be seen below in Figure 9.

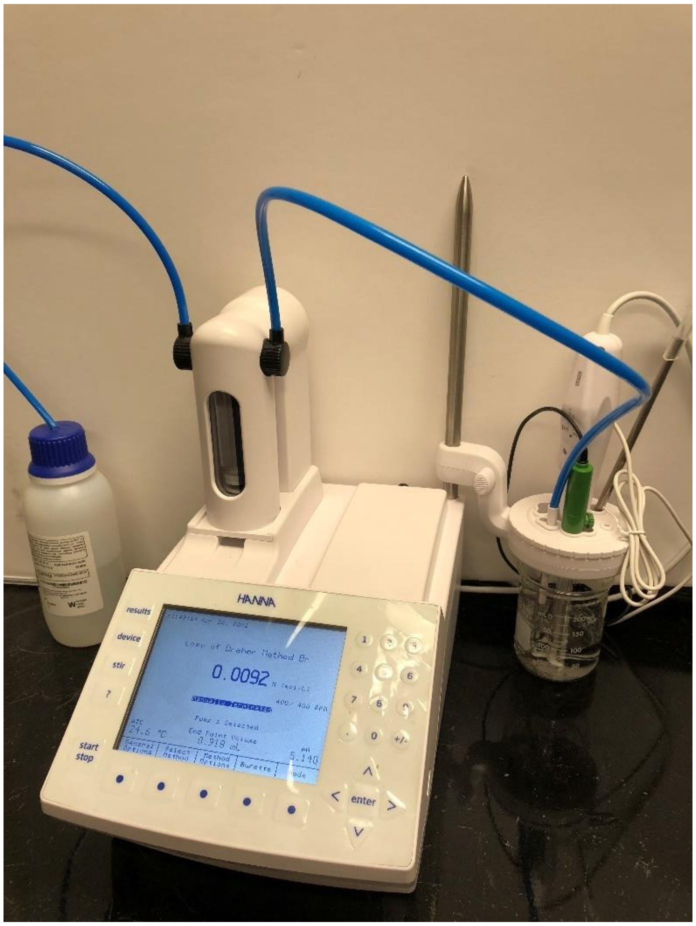


Figure 9: *Setup for titrations conducted with the potentiometric titrator, Hanna Instruments HI931.*

A full list of glass wear and supplies need to perform the titrations is shown below:

- Dry chemical balance with 0.001g accuracy
- Potentiometric titrator (Hanna Instruments #HI931)
- Two 150 ml beakers
- 2000 ml volumetric flask
- pH meter connected to the potentiometric titrator
- 100 ml graduated cylinder
- Cylinder of pure CO_2 gas
- Cylinder of pure N_2 gas
- Rotameter able to mix CO_2 gas to 1 mol %

5.2 Experimental Procedure

Stock solutions were created to a mass of 1000 g in a volumetric flask where the concentrations of the species varied from 0.025-0.0017 M (1525-100 ppm_w HCO_3^-). The concentrations of 0.025-0.0085 M were chosen to reflect a wide range of alkalinity values reported in water chemistry documentation from the industry. The titrant was a 1 N HCl stock solution from a chemical supplier (Fisher Scientific) and was used for all titrations conducted. The titrant concentration is high enough to generate data that can be used to accurately identify equivalence points.

The use of a potentiometric titrator is crucial to the accurate determination of equivalence point. The titrator has the ability to automatically adjust the volume of added titrant (larger additions at the beginning of the titration and smaller additions near the equivalence point) thus increasing the accuracy of measurements while collecting all the required data in a relatively short time. Titrations were performed mostly using the Rice methodology but some are repeated without CO_2 sparge, following a more standard acid/base titration method (referred to here as the Henderson methodology). Pros and cons of each methodology are discussed.

Species that are analyzed include NaOH, $NaHCO_3$, CH_3CH_2COONa, CH_3COONa, and HCOONa, where each was weighed separately prior to adding to the solution. Once the species being analyzed are added to the flask (after recording the added mass of each species), the flask is filled with deionized water to 1000 g total mass. To conduct titration properly, there cannot be solid precipitates present in the solution. Following the Rice methodology, the samples are then allowed to reach equilibrium with the sparge gas, set with a fixed pCO_2 being studied, using a sparging filter at a flow rate of 1 L/min for 30 min. If CO_2 was not used during titration (following the Henderson methodology), the sample was simply titrated following the preparation of the liquid sample – in this case, the titration was performed before the liquid sample could ever reach equilibrium with atmospheric CO_2. As mentioned earlier, the titration is then performed using 1 M HCl and data of pH *vs.* volume of acid added is recorded until a pH of 2 is reached. The amount of acid to reach the equivalence point can be anticipated when the total alkalinity of the liquid sample is known in advance.

5.3 Details of Potentiometric Titrator Methods

The potentiometric titrator allows for the collection of much more accurate data and analysis. It is an excellent tool for streamlining titrations over a wide range of titrand concentrations, avoiding experimental errors associated with hand (a.k.a. non-automated) titrations. Yet, the titration parameters have to be defined carefully to avoid generating systematic errors. The titrator can be programed to perform the titration up to a set pH, chosen by the operator. If the choice of the final pH is incorrect, it could cause the alkalinity to be underestimated.

Operation of the titrator is done using a signal stability mode in which the instrument waits a set time interval (Δt) during which the potential of the titrand solution is measured in solution (mV) is confined inside the potential interval (ΔE). The new signal value is acquired if the stability condition is reached after the minimum wait time (t_{min}). If the stability condition is not reached and the maximum wait time (t_{max}) has elapsed, the potential of the titrand is taken anyway and converted to a pH measurement. Signal stability mode allows for large additions of titrant to be added in the buffering region of the curve and smaller additions near the equivalence point.

The signal stability mode is referred to as a fast titration mode in this document. The fast titration mode is recommended to be used with the Henderson methodology and can be used with the Rice methodology at higher partial pressure sparges ($pCO_2 > 0.01$ bar). If titration data is collected too quickly under the signal stability mode, the solution will not have a chance to reach equilibrium at the constant sparge conditions. The collected titration data will then typically underestimate the pH of the titrand at higher pH values, as shown in Figure 10.

The titrator can also be programed to do what is referred to as a slow titration method. The slow titration method sets the titrator to perform the same stability mode but only adds titrant every 60 seconds. The wait time of 60 seconds between titration addition allows for equilibrium to establish itself within the solution before a pH measurement is taken. The slow titration method is used with the Rice methodology with low partial pressure sparges (pCO_2 <0.01 bar). The slow titration method is not ideal because of the time it takes to equilibrate the sample and conduct the titration (rate of 1 data point/min). The advantage of slow titrations is that they provide higher resolution data for comparison with the Rice equation. Figure 10 is an example of a slow titration conducted with this method under a constant sparge.

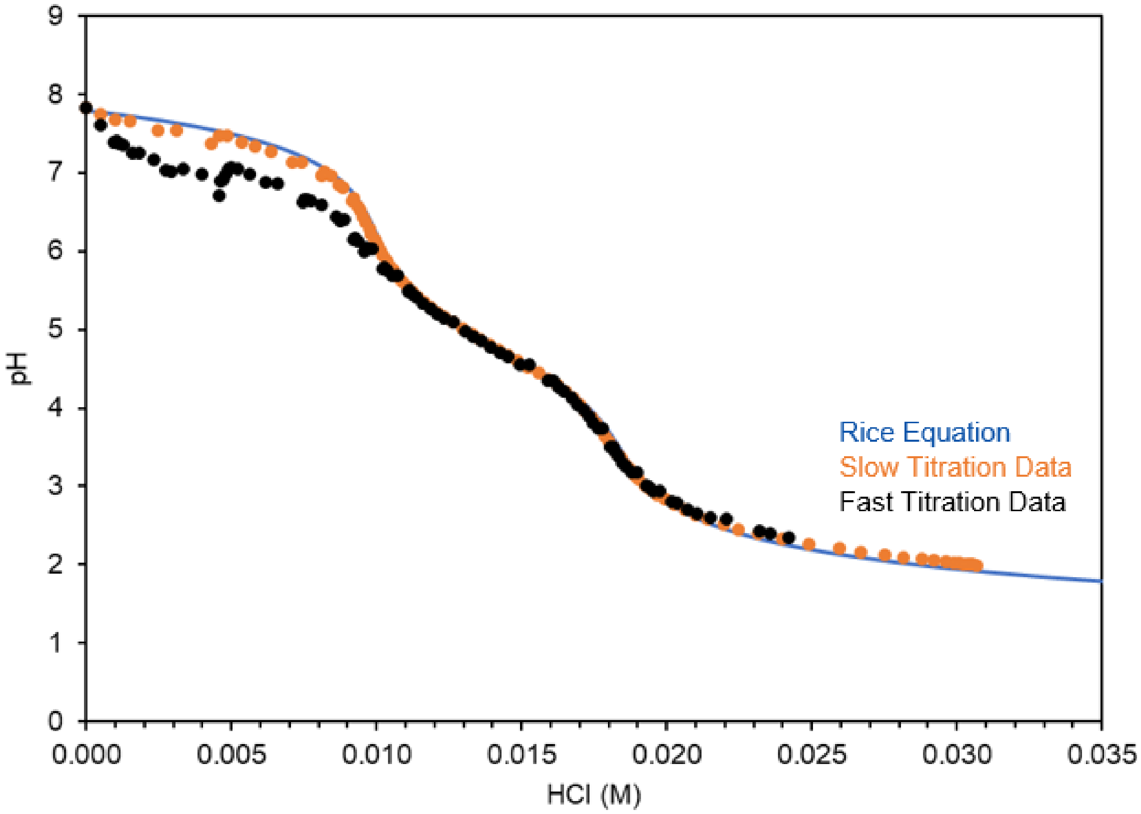
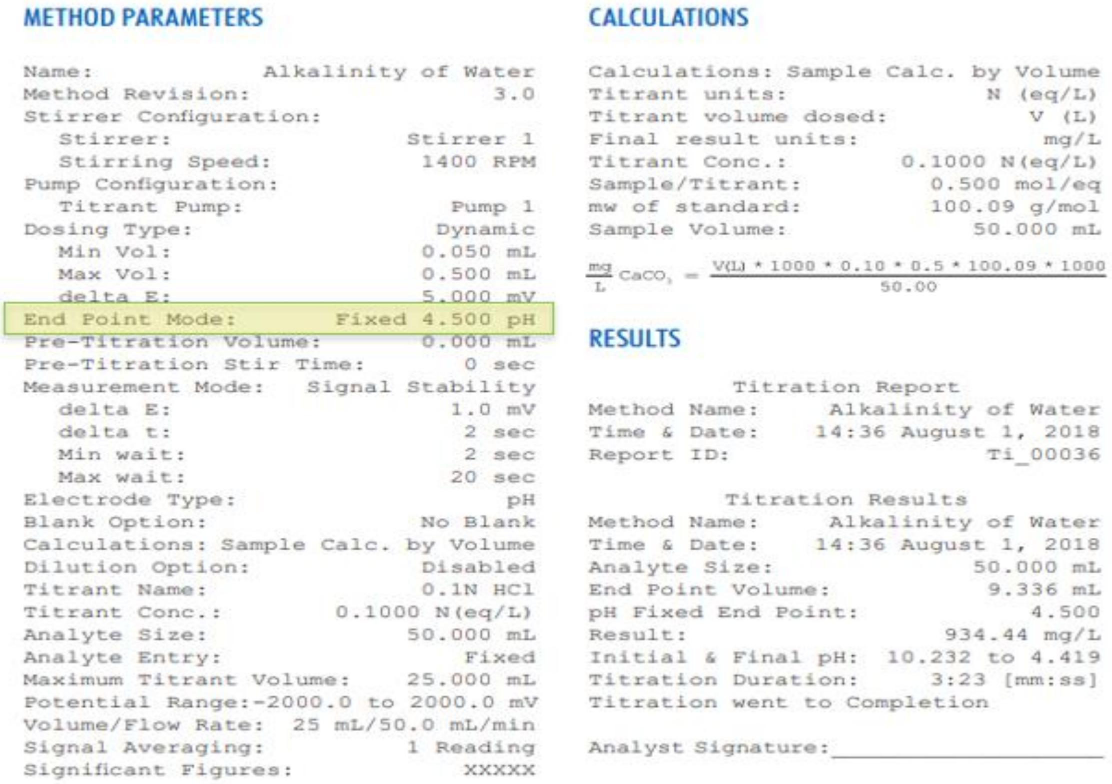


Figure 10: *Effect of data collection rate on titration results with an Aqueous sample of 0.01 M* $NaHCO_3$ *and 0.0085 M* CH_3COONa*, under constant sparge conditions of 0.01 bar* CO_2*.*

5.4 Recommended Modifications to Default Methods to Avoid Missing Equivalence Points

The titrator comes with twelve preloaded default titration methods to be used. One of these methods, labeled “Alkalinity of water 0-2500 mg/L $CaCO_3$, pH 4.5”, is a preloaded method for determination of total alkalinity in water by titration of a sample to a pH value of 4.5 [20] as shown in Figure 11. The alkalinity is reported in mg/L (ppm_w) as calcium carbonate. This method is meant to be the default one for titration of aqueous samples containing HCO_3^-, yet, the true alkalinity would not be measured correctly if organic acids were present. Of course, custom methods can be developed to cater for specific end point pH (and sampling rates). Doing so, however, can only come with the appropriate knowledge of the brine composition. Without a critical review of the parameters involved and the methods presented on potentiometric titrators, incorrect values can easily be obtained.



METHOD PARAMETERS

```
Name:                 Alkalinity of Water
Method Revision:                      3.0
Stirrer Configuration:
   Stirrer:                     Stirrer 1
   Stirring Speed:               1400 RPM
Pump Configuration:
   Titrant Pump:                   Pump 1
Dosing Type:                      Dynamic
   Min Vol:                      0.050 mL
   Max Vol:                      0.500 mL
   delta E:                      5.000 mV
End Point Mode:          Fixed 4.500 pH
Pre-Titration Volume:            0.000 mL
Pre-Titration Stir Time:            0 sec
Measurement Mode:   Signal Stability
   delta E:                        1.0 mV
   delta t:                         2 sec
   Min wait:                        2 sec
   Max wait:                       20 sec
Electrode Type:                        pH
Blank Option:                    No Blank
Calculations: Sample Calc. by Volume
Dilution Option:                 Disabled
Titrant Name:                    0.1N HCl
Titrant Conc.:            0.1000 N(eq/L)
Analyte Size:                   50.000 mL
Analyte Entry:                      Fixed
Maximum Titrant Volume:     25.000 mL
Potential Range:-2000.0 to 2000.0 mV
Volume/Flow Rate:  25 mL/50.0 mL/min
Signal Averaging:               1 Reading
Significant Figures:                XXXXX
```

CALCULATIONS

```
Calculations: Sample Calc. by Volume
Titrant units:                  N (eq/L)
Titrant volume dosed:              V (L)
Final result units:                 mg/L
Titrant Conc.:            0.1000 N(eq/L)
Sample/Titrant:            0.500 mol/eq
mw of standard:            100.09 g/mol
Sample Volume:                 50.000 mL
```

$$\frac{mg}{L} CaCO_3 = \frac{V(L) * 1000 * 0.10 * 0.5 * 100.09 * 1000}{50.00}$$

RESULTS

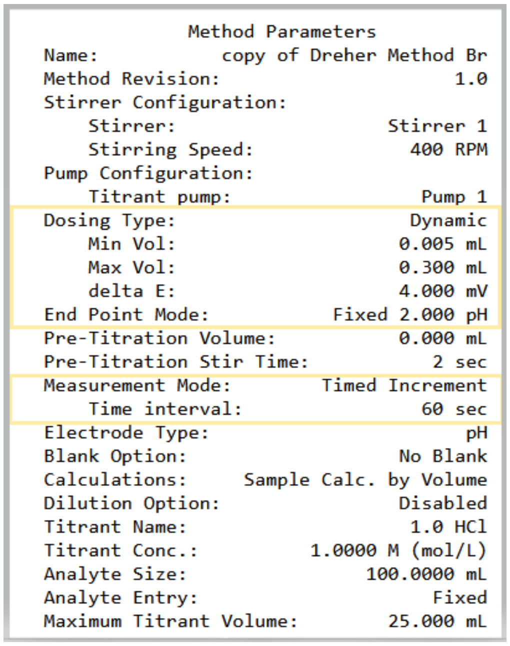
```
           Titration Report
Method Name:      Alkalinity of Water
Time & Date:    14:36 August 1, 2018
Report ID:                   Ti_00036

          Titration Results
Method Name:      Alkalinity of Water
Time & Date:    14:36 August 1, 2018
Analyte Size:               50.000 mL
End Point Volume:            9.336 mL
pH Fixed End Point:             4.500
Result:                   934.44 mg/L
Initial & Final pH: 10.232 to 4.419
Titration Duration:      3:23 [mm:ss]
Titration went to Completion

Analyst Signature:___________________
```

Figure 11: *Default method for the measurement of alkalinity “Alkalinity of water samples 0 to 2500 mg/L $CaCO_3$, pH 4.5 Endpoint”[*20*].*

Developing a custom method typically involves adjustment of several parameters, including the measurement mode (depending on the method used) and the endpoint of titration. Two separate measurement modes were used in this research for titrations: a signal stability mode for fast titrations and a timed increment for slow titrations. The minimum volume, maximum volume, and potential intervals to the titrand can adjusted to improve the quality of the data. To avoid missing equivalence points, the titrator is set to an end point titration of pH 2. The changes to the default method are outlined in Figure 12.



```
                 Method Parameters
Name:                copy of Dreher Method Br
Method Revision:                          1.0
Stirrer Configuration:
    Stirrer:                        Stirrer 1
    Stirring Speed:                   400 RPM
Pump Configuration:
    Titrant pump:                      Pump 1
Dosing Type:                          Dynamic
    Min Vol:                         0.005 mL
    Max Vol:                         0.300 mL
    delta E:                         4.000 mV
End Point Mode:                Fixed 2.000 pH
Pre-Titration Volume:                0.000 mL
Pre-Titration Stir Time:                2 sec
Measurement Mode:             Timed Increment
    Time interval:                     60 sec
Electrode Type:                            pH
Blank Option:                        No Blank
Calculations:          Sample Calc. by Volume
Dilution Option:                     Disabled
Titrant Name:                         1.0 HCl
Titrant Conc.:               1.0000 M (mol/L)
Analyte Size:                     100.0000 mL
Analyte Entry:                          Fixed
Maximum Titrant Volume:             25.000 mL
```

Figure 12: *Modified method used for the measurements of alkalinity in unknown samples and oil/gas field brines following the Rice method.*

5.5 Comparison Between Titration Data and Models Prediction

As much as possible, every set of experimental titration data is compared with model predictions – the Rice equation is used when the titration is done following the Rice methodology (*i.e.* with CO_2 sparging), while the Henderson equation is used for any other conditions (*i.e.* when equilibrium with atmospheric CO_2 is not met). Many of the titrations performed in this work are done following the Rice methodology. When performing titrations of samples of known composition, the required model input data (total alkalinity, organic acid content, ionic strength, pCO_2, temperature) are simply entered in the relevant equation, which is then plotted together with the experimental data. Comparison between experimental and modeling data are useful even at that point as it can highlight possible errors in the experimental methodology. When dealing with ideal solutions (*i.e.* ionic strength below 0.2 M), no fitting or adjustment of any of the constants implemented in the Rice equation was needed. For these cases, there was always a very reasonable agreement between the predictions obtained with the Rice or Henderson equations and the experimental data. However, when dealing with strongly non-ideal solutions (*i.e.* ionic strength above 0.2M), some discrepancies between modeling and experimental results were observed. In these cases, some curve fitting may be required, which is discussed in more details in Chapter 6.1.4.

In actual field cases, when a brine sample of unknown composition is being titrated, the visualization of experimental titration data may not enable the clear identification of equivalence points. In this case, fitting the Rice (or Henderson) equations to the experimental data is needed for the interpretation. This section describes the method used for curve fitting of titration data to the Rice or Henderson equation. First, the titration data were filtered to eliminate any data point corresponding to a pH below 3. Then, the Rice equation (or Henderson equation) was fitted to the titration data considering total alkalinity and concentration of carboxylate species as unknowns (pCO_2, temperature, ionic strength values are considered known parameters in a laboratory environment). The fitting was done using a non-linear regression method with minimizing the sum of the squares of the differences between experimental and modeling data (the built-in Excel® solver function was used successfully for that effort). When dealing with solutions with low ionic strength, this fitting exercise was quite successful, even with considering that all activity coefficient equal to one. Yet, with brines of high salt contents, deviations were observed even when using the correct values for activity coefficients. Curve fitting considering the correction parameters introduced in the Rice equation may be necessary in this case. However, this effort would require performing non-linear regression on four or five unknown parameters, thus increasing greatly the uncertainty on the calculated carboxylate concentration and the total alkalinity.

5.6 Determination of Equivalence Point using the d(pH)/d(C) Method

The determination of the equivalence points from visualizing the pH vs. $C_{titrant}$ curve is often difficult and prone to reading errors. Instead, it is common practice to plot d(pH)/d(C) vs. $C_{titrant}$, since the maxima of these curve do correspond precisely to the equivalence points. Using experimental data points, the d(pH)/d(C) vs. $C_{titrant}$ curve is obtained through Equation 12:

$$\frac{d(pH)}{d(C)} = \left(\frac{pH_x - pH_{x+1}}{C_x - C_{x+1}}\right) \qquad \text{Equation 12}$$

Yet, the accuracy of this method depends greatly on the data resolution, which is often too low at the equivalence point, when large changes in pH are recorded with only very small addition of titrant. In order to address this limitation, the titration conditions are first simulated using the Rice (or the Henderson) equations, enabling the generation of a large number of data points. After making sure that the fit between experimental and modeling data is correct, Equation 12 is then applied to the modeled data. This way, very clear maxima of the d(pH)/d(C) *vs*. $C_{titrant}$ curve can be obtained, minimizing errors in the interpretation of the data.

An example of this methodology is shown in Figure 13 and Figure 14. Figure 13 presents the experimental titration data together with the corresponding curve created by using the Rice equation. A good match between the two sets of data is clear. The sample conditions include bicarbonate and carboxylate ions, which make the inflection points relatively shallow and difficult to determine with high accuracy. Figure 14 presents the d(pH)/d(C) vs. $C_{titrant}$ curve corresponding to the data generated with the Rice equation – equivalence points are very easily determined, showing the usefulness of this method.

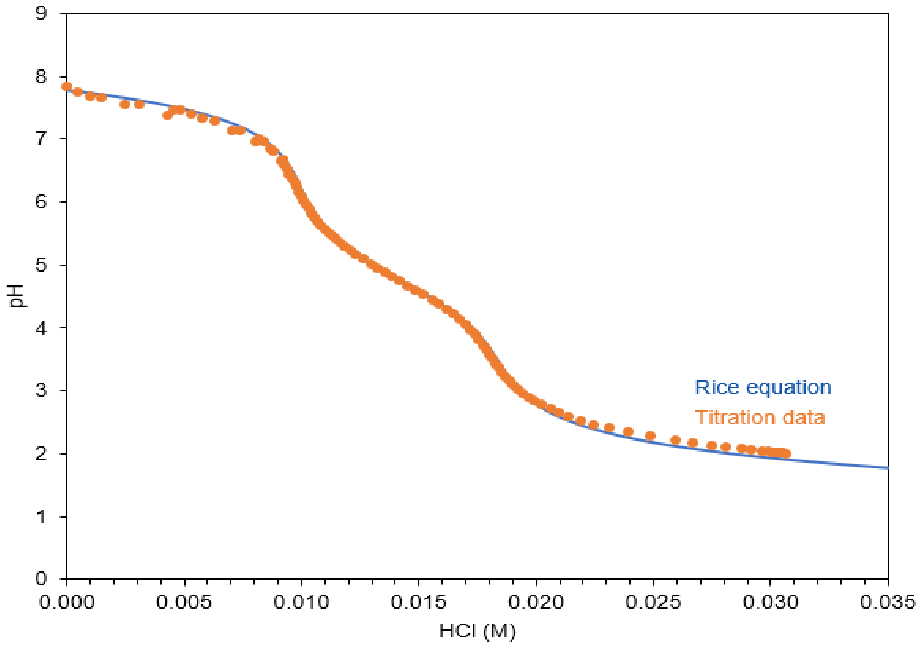


Figure 13: *Comparison between modeling data using the Rice equation and experimental titration data (100 ml): 0.01 M* $NaHCO_3$ *and 0.0085 M* CH_3COONa*.*

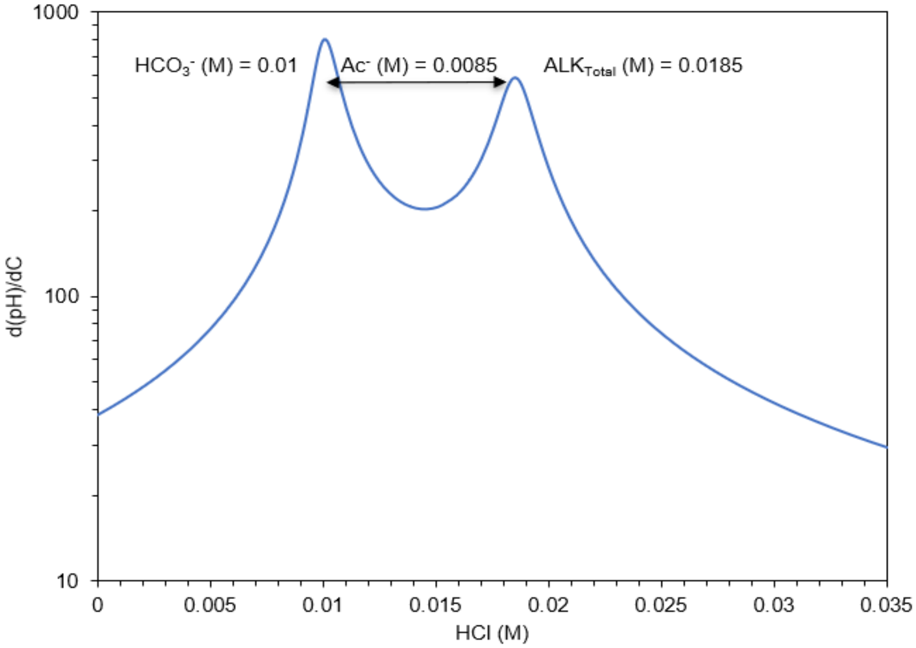


Figure 14: *d(pH)/d(C) curve derived from the modeled data using the Rice equation for a titration of a 100 ml aqueous sample 0.01 M* $NaHCO_3$*, 0.0085 M* CH_3COONa*, 0.01 bar* CO_2*.*

Chapter 6: Results and Discussion

6.1 Rice Methodology: Effect of Operating Parameters on Titration

The effects of different operating parameters on the titration results are studied in this section. All titrations are done following the Rice methodology – *i.e.* with constant sparging of CO_2 gas – unless specified. The operating parameters of interest include the concentrations of $NaHCO_3$, CH_3COONa, type of organic acids, ionic strength, and type of salt species. The analysis is focused on the shape of the pH *vs.* $C_{titrant}$ curve, the comparison with modeling, and the ease of identification of equivalence points. In addition, in an effort to update and in some cases simplify the methodology, the effect of titrant addition rate, CO_2 sparging, and partial pressure of CO_2 (from 0.01-1 bar) are also discussed.

6.1.1 Effect of pCO_2 on Titration of Solutions Containing $NaHCO_3$ and CH_3COONa

This set of titrations aim at investigating the effect of CO_2 sparging pressure on the titration of an aqueous solution containing 0.01 M $NaHCO_3$ and 0.0085 M CH_3COONa. The choice of concentration values is arbitrary are representative of field conditions and is kept consistent throughout this test series. Three sparging CO_2 pressures are considered: 1, 0.1 and 0.01 bar. Sparging with CO_2 does not affect the total alkalinity, which is set to 0.0185 M, but is expected to affect the shape of the titration curve and facilitate the identification of equivalence points. In addition, the Rice methodology itself mentions a partial pressure of 0.01 bar CO_2 to be used during titration.

The first titration is done with a sparging CO_2 pressure of 1 bar. Two trials are conducted using fast titration and signal stability mode. The use of fast *vs* slow titration is discussed in Chapter 5:Experimental Procedure and Testing Equipment. In this case, fast titration gives acceptable results as the experimental titration data, shown in Figure 15, are similar to the modeled data calculated with the Rice equation. An excellent match is obtained over the entire pH range, showing that equilibrium is reached rapidly and that there is no need to slow the data collection rate (*i.e.* no need to switch to slow titration). Error between the two experimental trials is relatively small and is calculated, using the difference between the two measured values of total alkalinity, to be $3.25 \times 10^{-4} M$ or 2%. The modeled titration curve (and the experimental data) only shows one inflection point, corresponding to the total alkalinity of the sample, while two inflection points were expected, one for $NaHCO_3$ and another for the CH_3COONa. However, the relative contribution of $NaHCO_3$ and CH_3COONa is not visible. This is due to the 1 bar CO_2 sparge which leads to a low initial pH (slightly below 6 in these conditions), causing the alkalinity contribution due to $NaHCO_3$ to be indistinguishable on the plot. This observation is reinforced by the plot of d(pH)/d(C) *vs.* concentration of titrant added, generated from the modeled data, as shown in Figure 16. The maximum associated with the total alkalinity is clearly seen but the contribution due to $NaHCO_3$ is hard to identify. It is consequently difficult to separate the contribution of the bicarbonate species from the total alkalinity. Ideally, titration parameters should be set to ensure that the maxima associated to $NaHCO_3$ and total alkalinity should be easily identifiable, the difference between these two peaks being equivalent to the carboxylate species (in this case

CH_3COONa) contribution. Therefore, it is not recommended to conduct titrations under a 1 bar CO_2 sparge as it does not allow for easy separation of the species contributions to alkalinity. A lower sparging pressure is recommended.

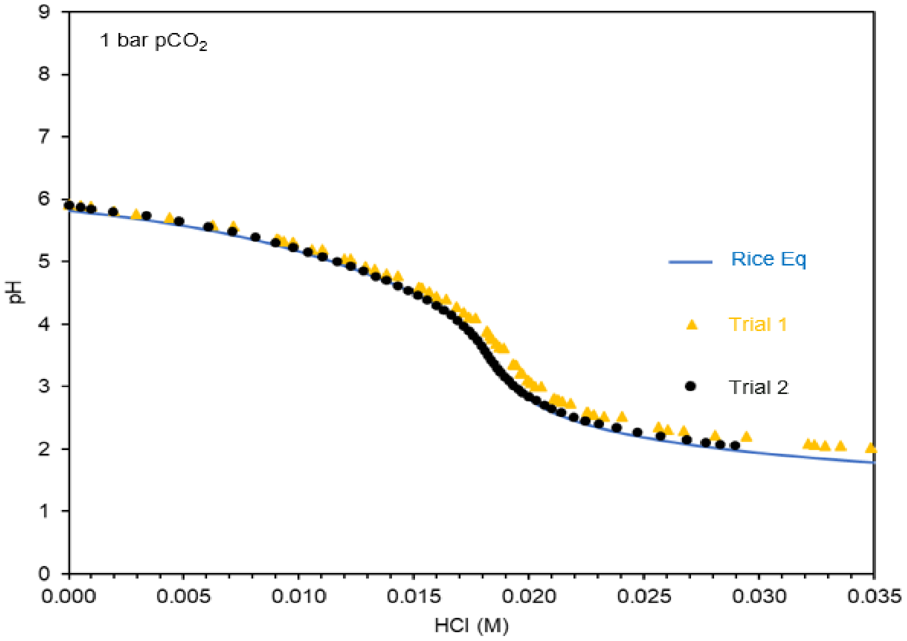


Figure 15: *Aqueous samples of 0.01 M $NaHCO_3$ and 0.0085 M CH_3COONa, compared to calculated values from the Rice equation under constant sparge of 1 bar CO_2.*

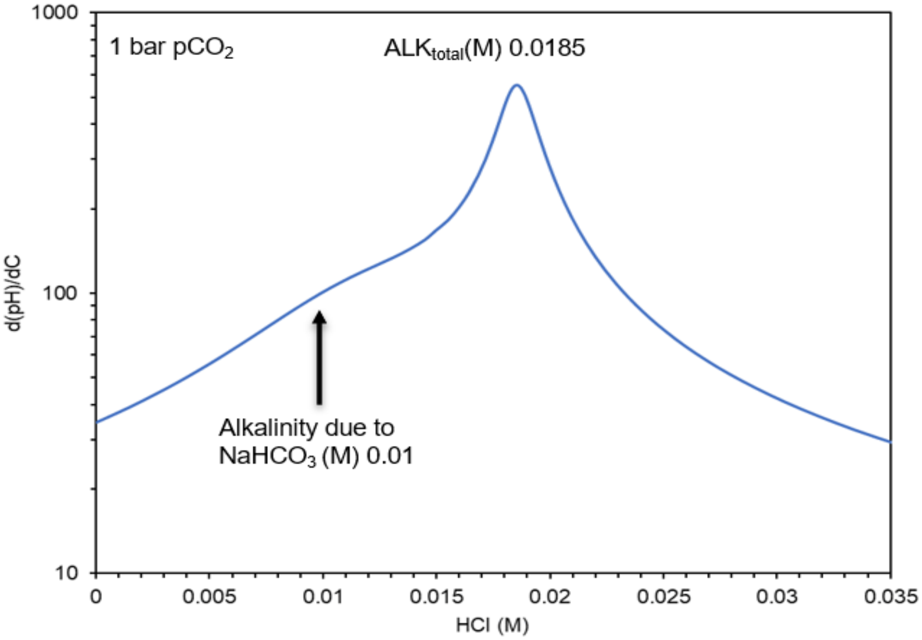


Figure 16: *The d(pH)/d(C) curve for a titration of aqueous sample containing 0.01 M* $NaHCO_3$*, 0.0085 M* CH_3COONa*, 1 bar* CO_2 *from Rice equation model (Figure 15).*

The next experimental titration (and its repeat) was conducted with a constant CO_2 sparge of 0.1 bar (using N_2 as completing gas), again with a fast titration using the signal stability mode. The same base solution was used, consisting of 0.01 M $NaHCO_3$ and 0.0085 M CH_3COONa with a total alkalinity of 0.0185 M. The titration data collected shown in Figure 17 is compared with the modeled data using the Rice equation over the entire pH range. Error between the two trials is calculated using the difference between the two measured values of total alkalinity and is found to be 3.75×10^{-4} or 2%. The pH vs. $C_{titrant}$ does show two inflection points, which is an improvement from the previous experimental titration data obtained at 1 bar pCO_2. However, the changes in slope of the curve are still quite shallow and it is difficult to determine the equivalence points with accuracy. The modeled Rice equation was then used to generate a plot of d(pH)/d(C) vs. $C_{titrant}$, as shown in Figure 18. The contribution of $NaHCO_3$ to the total alkalinity is visible in the first maximum, yet it is not very sharp. This could still lead to difficulties separating the contribution of the bicarbonate and acetate ions to the total alkalinity. Testing an even lower CO_2 sparge pressure is of interest as it could yield even sharper peaks in the d(pH)/d(C) *vs*. $C_{titrant}$ plot.

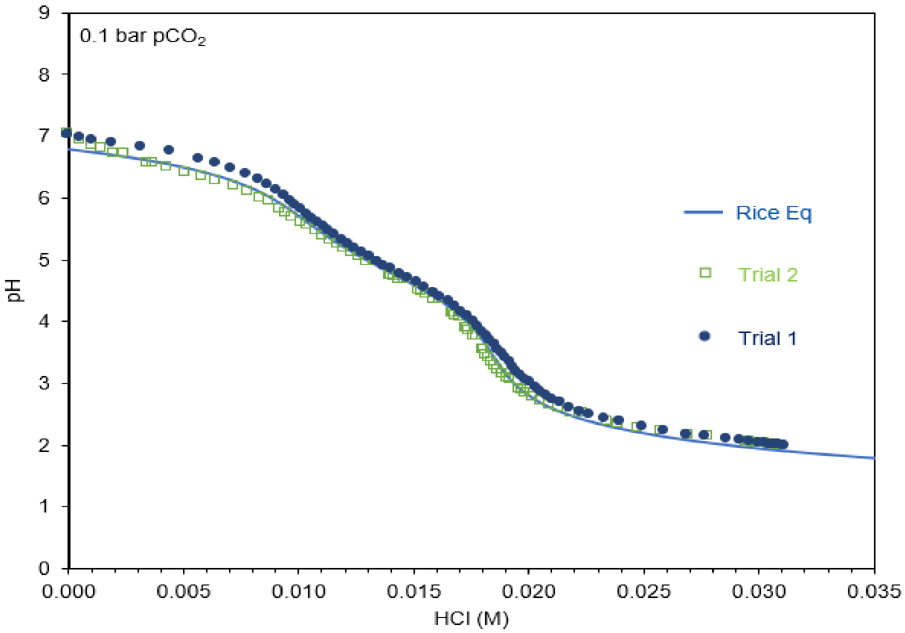


Figure 17: *Aqueous samples containing 0.01 M* $NaHCO_3$ *and 0.0085 M* CH_3COONa*, compared to calculated values from the Rice equation under constant sparge of 0.1 bar* CO_2*.*

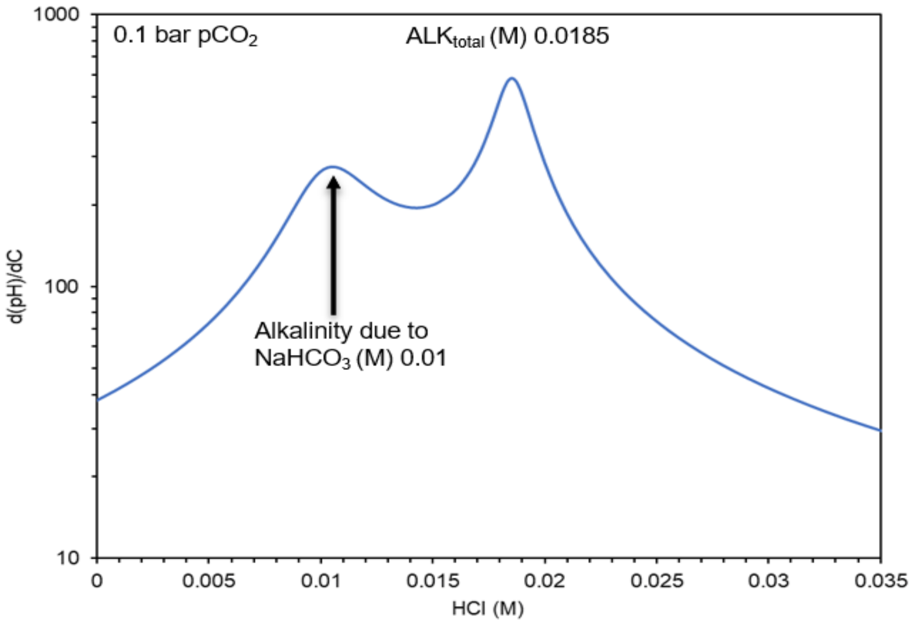


Figure 18: *The d(pH)/d(C) curve for a titration of aqueous sample containing 0.01 M* $NaHCO_3$*, 0.0085 M* CH_3COONa*, 0.1 bar* CO_2 *modeled with Rice equation (Figure 17).*

The last set of experimental titrations was done at a CO_2 sparging pressure of 0.01 bar (N_2 being used as completing gas). The same base solution consisting of 0.01 M $NaHCO_3$ and 0.0085 M CH_3COONa with a total alkalinity of 0.0185 M was used. The two repeats conducted for this condition, as shown in Figure 19, were performed using two different data collection rates. The first trial was conducted with a fast titration using the signal stability mode, while the second trial used the slow titration method. In this condition, the data modeled using the Rice equation agree better with the experimental data obtained with the slow titration. The discrepancy is visible at the high pH range, while the HCO_3^- is being titrated, suggesting that with a CO_2 sparge pressure of 0.01 bar, chemical equilibrium with the gas phase may take longer to be reached and that a slower data collection rate is needed. This agrees well with literature published on the Rice methodology [28] which also recommend "slow" titration when using a CO_2 sparge pressure of 0.01 bar with a gas flow rate of 1 liter/min. Below pH 6, the slow and fast titration data give similar results which makes sense since past that point, carboxylate ions are being titrated. Another observation that can be made is the sharp change in slope on the experimental titration data, displaying very clear equivalence points. This is confirmed with the plot of d(pH)/d(C) *vs.* $C_{titrant}$ obtained for the modeling data, as shown in Figure 20. The contribution of CH_3COONa and $NaHCO_3$ to the total alkalinity can easily be separated. The maxima are very sharp and correspond with good accuracy to the concentrations initially added to the liquid sample. Therefore, it is recommended to conduct titrations with a 0.01 bar CO_2 sparge if separating the individual contributions of different species to total alkalinity is desired. The use of 0.01 bar CO_2 sparge gas agrees well with the literature associated with the Rice methodology. If the total alkalinity is the only output that is required from the titration, then the CO_2 sparge pressure is not relevant and gas sparge by itself is not even necessary. In this case, the Henderson methodology is sufficient, as shown later in Chapter 6.2.1, saving time and effort. The CO_2 sparge, however, does provide useful information about the presence and concentration of acetate species. In all cases, irrespective of the CO_2 sparge pressure, the experimental and modeling data clearly show that the titrations should be conducted until a pH of 2, in order to obtain an accurate determination of the total alkalinity. In addition, it is important to repeat that the use of CO_2 sparge does not affect the total alkalinity or even the contribution of $NaHCO_3$ to the total alkalinity. The effect is seen only on the shape of the pH vs. $C_{titrant}$ curve, at high pH above the first equivalence point (corresponding to HCO_3^-).

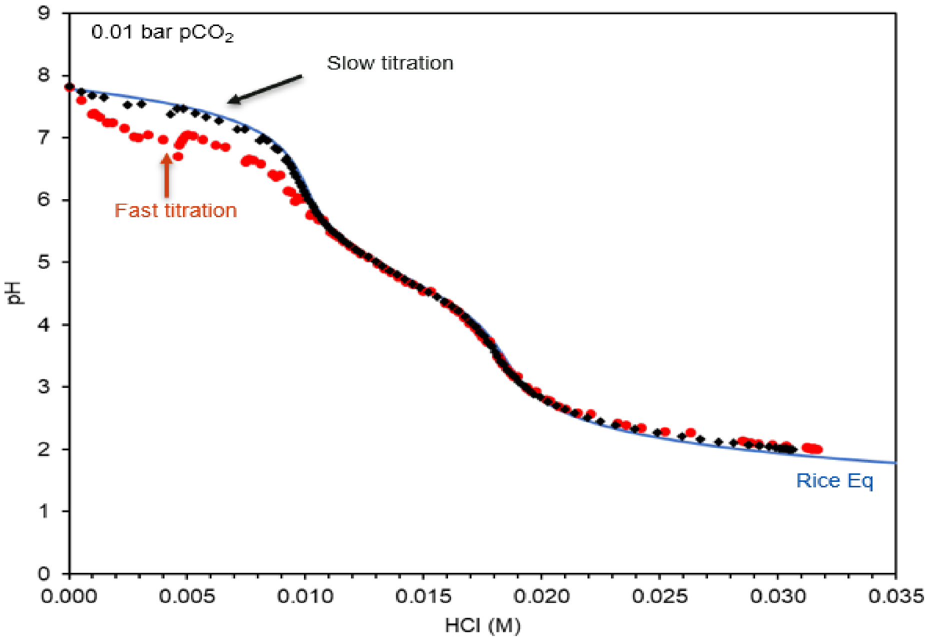


Figure 19: *Aqueous samples of 0.01 M* $NaHCO_3$ *and 0.0085 M* CH_3COONa*, compared to the Rice equation under constant sparge of 0.01 bar* CO_2*.*

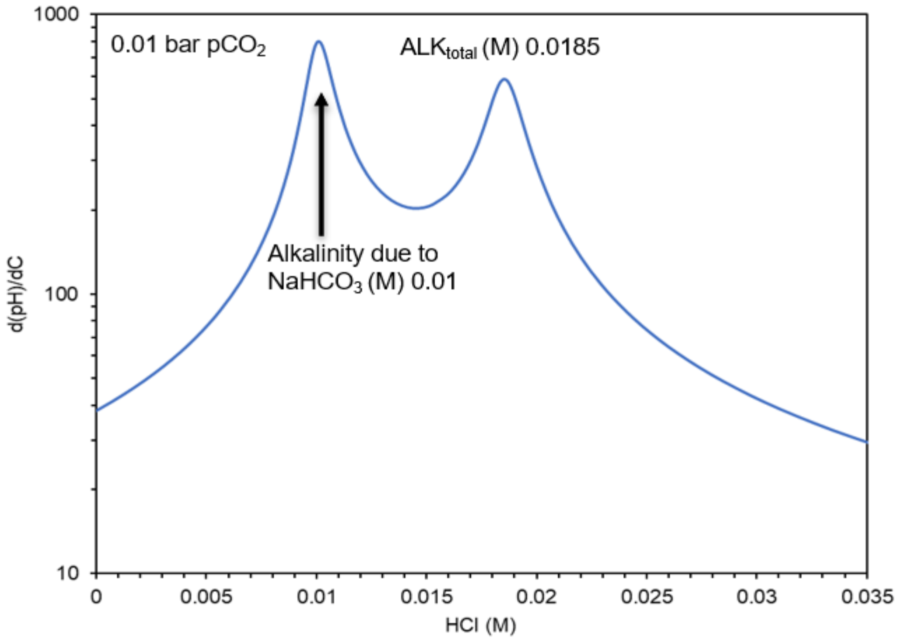


Figure 20: *The d(pH)/d(C) curve for a titration of aqueous sample containing 0.01 M* $NaHCO_3$*, 0.0085 M* CH_3COONa*, 0.01 bar* CO_2 *modeled with the Rice equation (Figure 19).*

The effect of sparging with nitrogen before and during titrations was studied to categorize the influence of the absence of CO_2. The following experimental titrations were done at a N_2 sparging pressure of 1 bar N_2 with a gas flow rate of 1 liter/min. A solution consisting of 0.01 M $NaHCO_3$ and 0.0085 M CH_3COONa with a total alkalinity of 0.0185 M was used. The two repeats conducted for this condition, as shown in Figure 21, were performed using a slow titration method. In this condition, the data modeled using the Rice equation using agree well with the experimental data obtained using an N_2 sparge. However, an equivalent partial pressure of 0.0005 bar had to be used as an input to the model to represent the pCO_2 in equilibrium with the water sample, since using 0 bar pCO_2 would yield results that would not match the experimental results. There was also a lot of variability in the measurement of pH when sparging with nitrogen.

Inconsistencies in the measurement originate from the inability to reach chemical equilibrium as the N_2 drives of the alkalinity species, and titrant is added. If an N_2 sparge was conducted for a long time, all carbonic species would leave the solution and the alkalinity would be held only through OH^-. It is not recommended to conduct titrations under N_2 sparge due to variability in the data and long titration times required.

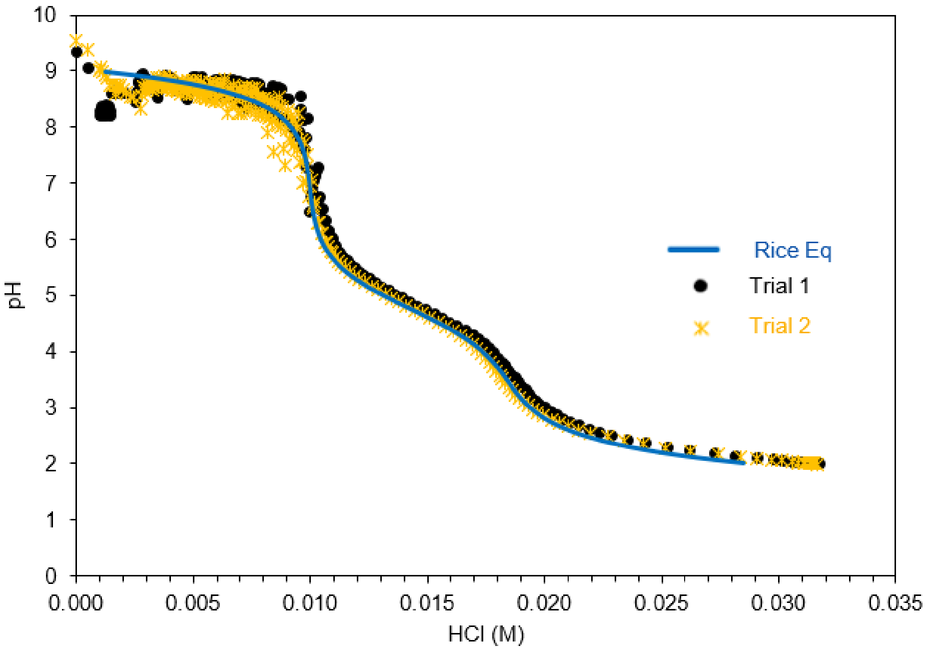


Figure 21: *Aqueous samples of 0.01 M* $NaHCO_3$ *and 0.0085 M* CH_3COONa*, compared to the Rice equation under constant sparge of 1 bar* N_2*.*

6.1.2 Effect of CH_3COONa Concentration on Titrations

6.1.2.1 Titrations of solutions containing $NaHCO_3$ under CO_2 sparge

This series of experimental titrations aims at characterizing the effect of CH_3COONa concentration on the shape of the titration curve, the main objective being to confirm that end point titration performed to pH 4.5 are inadequate in the presence of organic acid. Aqueous solutions made of various concentrations of CH_3COONa, ranging from 0 to 0.017M, but with a constant $NaHCO_3$ concentration of 0.01M, were investigated and prepared. As discussed above, this set of titrations were conducted under 0.01 bar CO_2 sparge conditions. The baseline solution (no acetate salts) contained a total alkalinity of 0.01 M and increasing concentration of CH_3COONa increased the value of total alkalinity. First, it should be noted that, in the absence of acetate, the equivalence point is very sharp and the pH vs. $C_{titrant}$ curve starts to change slope around pH 7 and then follows an almost vertical decline all the way to pH 3. In this case, ending the titration to pH 4.5, as ASTM 1067D suggests [20][21][22], would be sufficient to obtain an accurate reading of the total alkalinity. However, in the presence of CH_3COONa, as the pH decreases with the addition of HCl, the titration curves do not show such a sharp change in slope. A first equivalence point is noticeable between pH 7 and 6, which corresponds to HCO_3^- titration. The second equivalence point does not appear before pH 5.3. As expected, the influence of the HCO_3^- ion diminishes and the influence of CH_3COO^- takes over. The defined endpoint of titration for bicarbonate systems (pH 4.5), as referred to by as ASTM 1067D, is shown as a gray horizontal line in Figure 22. It is clear that determining the alkalinity at pH 4.5 is inadequate for systems containing carboxylate salts. Instead, it is recommended to complete the titration at least to pH 3.

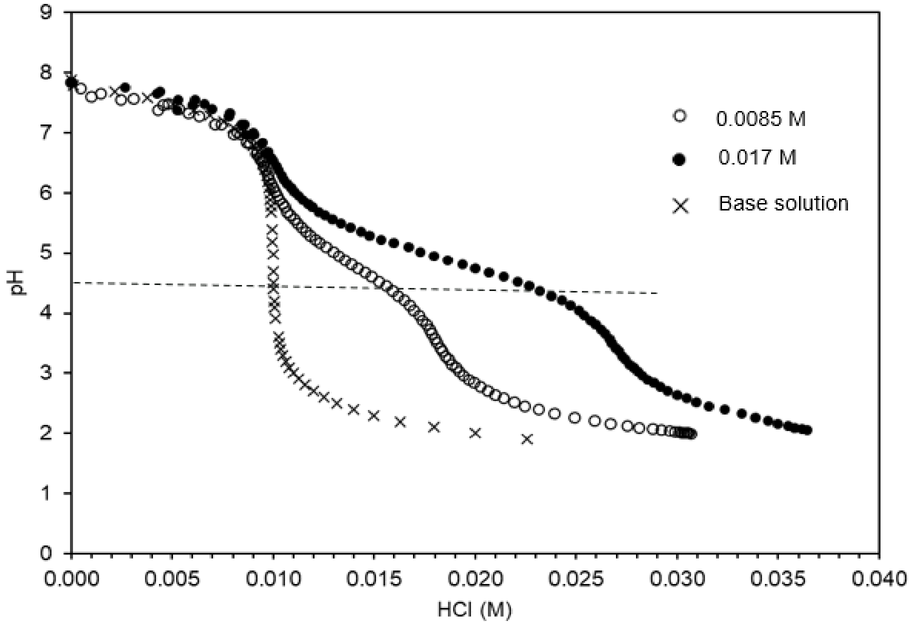


Figure 22: *Titration of aqueous samples containing concentrations of CH_3COONa 0.0085 and 0.017 M in 0.01 M $NaHCO_3$ solution, under constant sparge of 0.01 bar CO_2. Dotted horizontal line shows the endpoint at pH 4.5.*

6.1.2.2 Titrations of solutions containing $NaHCO_3$ without gas sparge

While the usefulness of using a CO_2 sparge has been demonstrated in the previous section, this method, in practice, is far from being common - instead titrations are often performed in atmospheric conditions without any gas sparging. Experimental titrations are performed in this section to highlight that point – they are conducted under atmospheric conditions and without any gas sparge. The solution contains concentrations of CH_3COONa ranging from 100-1000 ppm$_w$ (0.0017-0.017 M). The solutions are all prepared using the baseline solution of 0.1 M bicarbonate. The results are presented in Figure 23 and Figure 24. The first observation is that in the absence of CO_2 sparge, and in the presence of CH_3COONa, the inflection point associated with the titration of HCO_3^- is not visible on the graph. The second observation, which is in line with what is shown in

Figure 22, is that the equivalence point in the presence of acetate salts is only well-defined below pH 3.5. As a comparison, the defined endpoint of titration for bicarbonate systems recommended by ASTM 1067D (pH 4.5) is shown as a gray horizontal line in Figure 24.

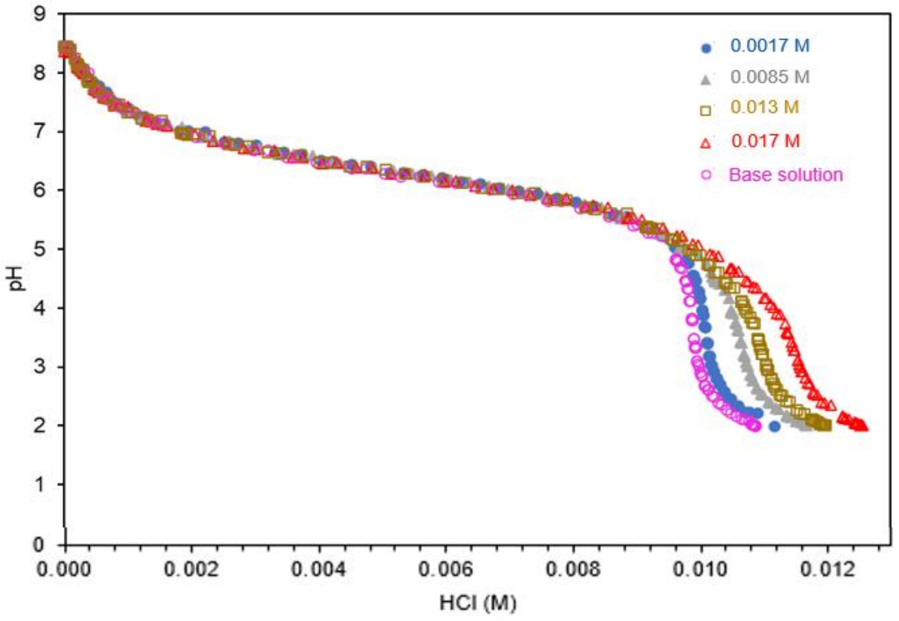


Figure 23: *Titration of aqueous samples containing concentrations of* CH_3COONa *(100-1000* ppm_w*/0.0017-0.0169 M) in 0.1 M* $NaHCO_3$ *solution, no gas sparging.*

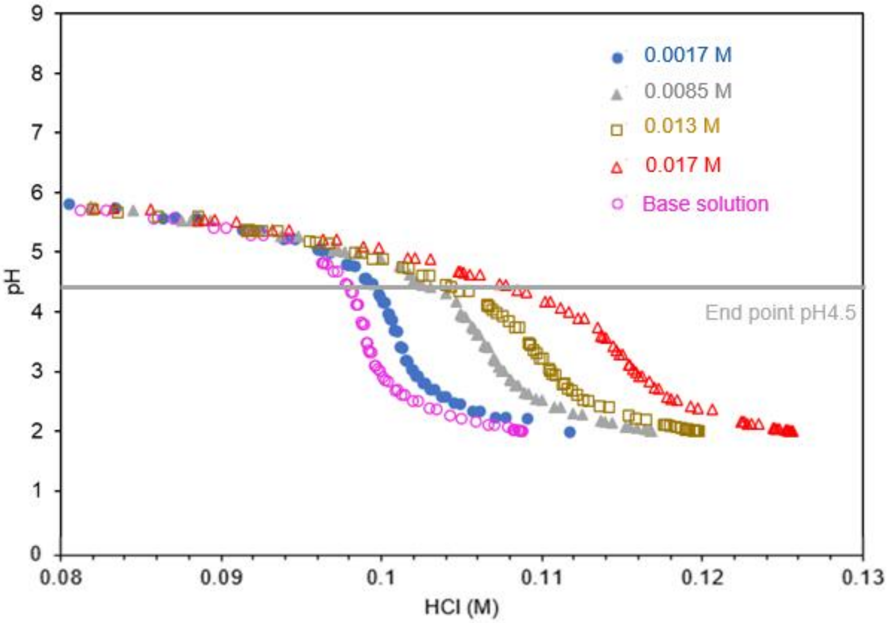


Figure 24: *Details of Figure 23 around the equivalence point - Titration of aqueous samples containing concentrations of CH_3COONa (100-1000 ppm_w/0.0017-0.0169 M) in 0.1 M $NaHCO_3$ solution, no gas sparging.*

The error that is generated by choosing the wrong endpoint pH is presented in a plot of measured total alkalinities (M) *vs.* total Ac^- (mM), shown in Figure 25. The pH values for equivalence point titrations were shown to be between 3.2-3.8 pH. The data collected indicates that increasing the concentration of acetate salts increases the error between endpoints at pH 4.5 and the equivalence point. The error between a titration conducted to a pH 4.5 endpoint and a titration conducted to the maximum d(pH)/d(C) range (at the equivalence point) is approximately 9 %.

In the field, it is very common that chemical analysis of brines not to include organic acid measurements. This means that operators are often not aware whether or not organic acid is present in the produced fluids. The method of using an endpoint titration with indicator or a single stopping point programmed on a titration apparatus would give a false value of alkalinity due to the equivalence point not being reached.

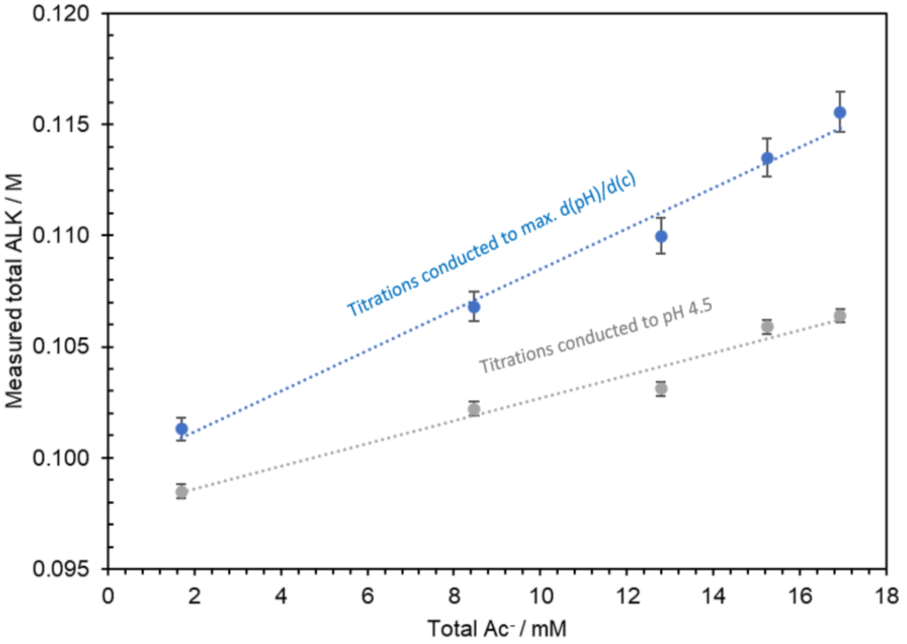


Figure 25: *Difference in total alkalinity at various organic acid concentrations (100-1000 ppm*$_w$*/0.0017-0.0169 M) in 0.1 M* $NaHCO_3$ *for endpoints at 4.5 pH (gray) and endpoints at the equivalence point (blue), under no gas sparge.*

6.1.2.3 Titrations of solutions without $NaHCO_3$

The presence of $NaHCO_3$ is omitted in this short section, which has only academic value since HCO_3^- ions are always present in oil and gas brines. Since the alkalinity comes entirely from CH_3COONa, gas sparging during these titrations is not necessary. Figure 26 compares two separate titrations of 0.0085 M CH_3COONa conducted with and without a constant 0.01 bar CO_2 sparge. The data shows little difference in the shape of the curve or the location of the equivalence point, as expected. The initial pH was expected to be much lower when CO_2 sparging was used, error in the initial pH value could be caused by a near neutral pH. The Henderson- Hasselbalch equation can be used to model titration conditions when no CO_2 sparge is conducted, as shown in Figure 26.

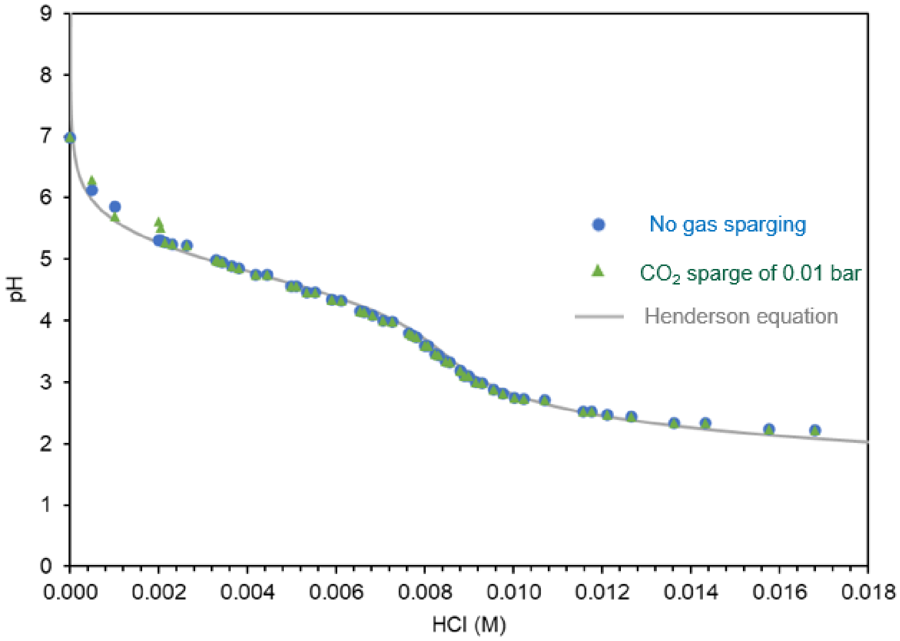


Figure 26: *Titration of aqueous samples containing 8.5mM* CH_3COONa *with 0.01 bar* CO_2 *sparge (blue dots) and without gas sparging (green triangles).*

6.1.3 Effect of the types of Carboxylate Salts on Titrations of Solutions Containing $NaHCO_3$

The aim of this section is to investigate if the type of carboxylate salts, commonly found in oil and gas brines, have an effect on the shape of the titration curve. Produced water from oil and gas field brines often contain many different carboxylate species in low concentrations. Carboxylate species with similar pK_a values have very similar inflection points and characteristics in titration. Three common carboxylate species are studied in this section: acetate, propionate, and formate. Propionic acid and acetic acid have very similar pK_a (4.74 for acetic acid and 4.88 for propionic acid at 25°C) and, consequently, titrations involving these two species should be similar. Formic acid has a lower pK$_a$ value than other organic acids (pK$_a$ of 3.7 at 25°C) and is classified as a more potent, or stronger, acid.

The Rice equation, as written in Equation 6, does not explicitly include terms for propionate and formate ions – it only considers acetate ions. However, it can be modified to account for these species. Since acetic acid and propionic acid have very similar pK$_a$, their contribution could be bundled up together. However, since formic acid has a significantly different pK$_a$ than other organic acids, a distinct additional term should be considered. Equation 13 presents how the Rice equation can be modified to account for the presence of propionate and formate salts. A publication written by the Rice University Brine Chemistry Consortium in 2019 made similar additions to the equation to represent the equivalent sum of molar concentrations of ammonia, borate, silica, and phosphate [29]

$$HCl(M, calc) = Alk + \frac{10^{-pH}}{\gamma^{H+}}$$

$$- \left[\frac{fHCO_3 * K_{1,H_2CO_3} * K_{CO_2} * P_{CO_2,gas} * \gamma_{g\,CO_2}}{10^{-pH} * \gamma_{HCO_3^-}} + \frac{TAc^-}{\frac{10^{-pH} * \gamma_{Ac^-}}{fAc * K_{HAc} * \gamma_{HAc,eq}} + 1} + \frac{K_w}{10^{-pH} * \gamma_{OH^-}} \right.$$

$$\left. + \frac{T_{CHOO-}}{\frac{10^{-pH} * \gamma_{CHOO-}}{f_{CHOO-} * K_{CHOOH} * \gamma_{CHOOH,eq}} + 1} + \frac{T_{CH_3CH_2OO-}}{\frac{10^{-pH} * \gamma_{CH_3CH_2OO-}}{f_{CH_3CH_2OO-} * K_{CH_3CH_2OO} * \gamma_{CH_3CH_2OO,eq}} + 1} \right]$$

Equation 13

Table 8: *Table of variables used in the Modified Rice Equation.*

Alk	Total Alkalinity (M)
TAc^-	Total Acetate (M)
T_{CHOO-}	Total formate (M)
$T_{CH_3CH_2OO-}$	Total propionate (M)
P_{CO_2}	CO_2 Partial Pressure (bar)
K	Equilibrium Constants
γ	Activity Coefficients
$fHCO_3^-, fAc^-$	Correction Factor for "true" activity coefficients ≈ 1

Figure 27 presents modeled titrations, calculated using the modified Rice equation, of aqueous solutions containing only either acetate, propionate or formate salts, at a fixed concentration of *0.0085 M*. The stronger acidic characteristic of the formate ion gives it a much shallower inflection with no obvious equivalence point. Experimental titration results involving only formate salts (solution consisting of 0.0085 M CHOONa), as shown Figure 28 and Figure 29, confirm this point. When modeling the titration characteristics of formate salts, the modified version of the Rice equation should be used to account for its specific characteristic.

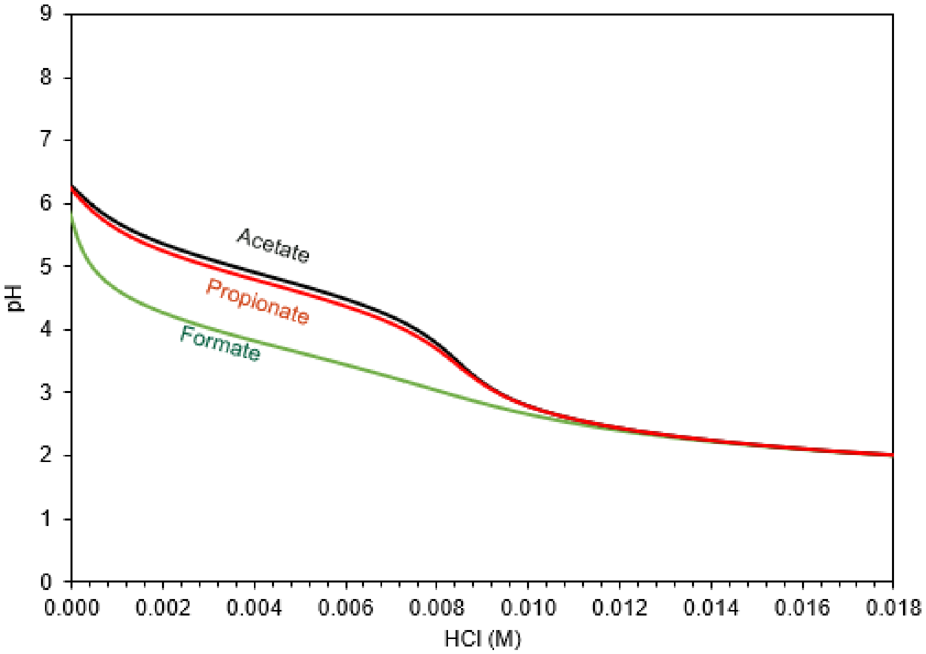


Figure 27: *Modeled titration curves of 0.0085 M acetate, propionate, or formate modeled with the modified Rice equation under constant sparge of 0.01 bar CO_2.*

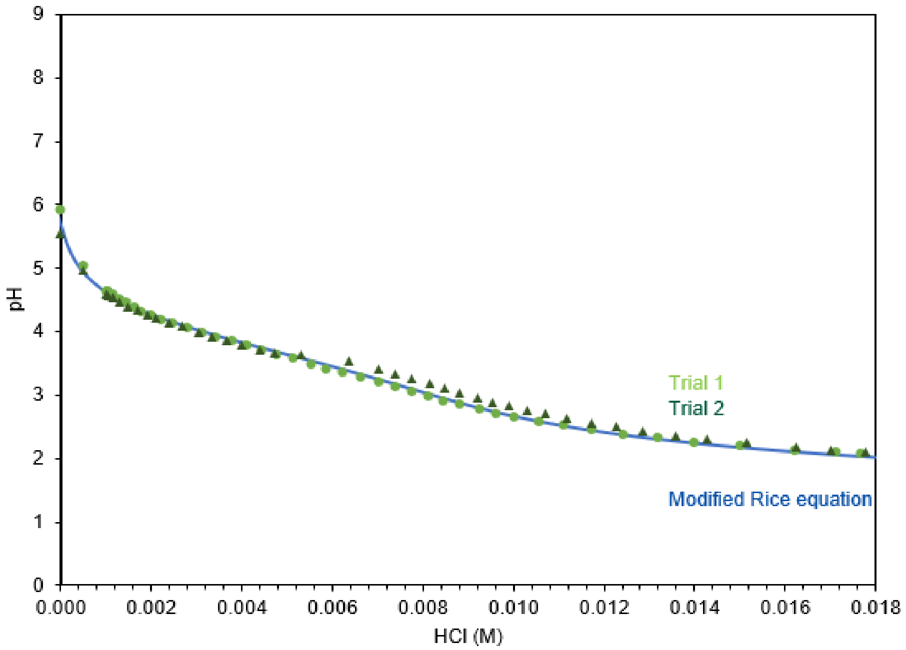


Figure 28: *Aqueous samples of 0.0085 M HCOONa, compared to the Modified Rice equation under constant sparge of 0.01 bar CO_2 (fast titration).*

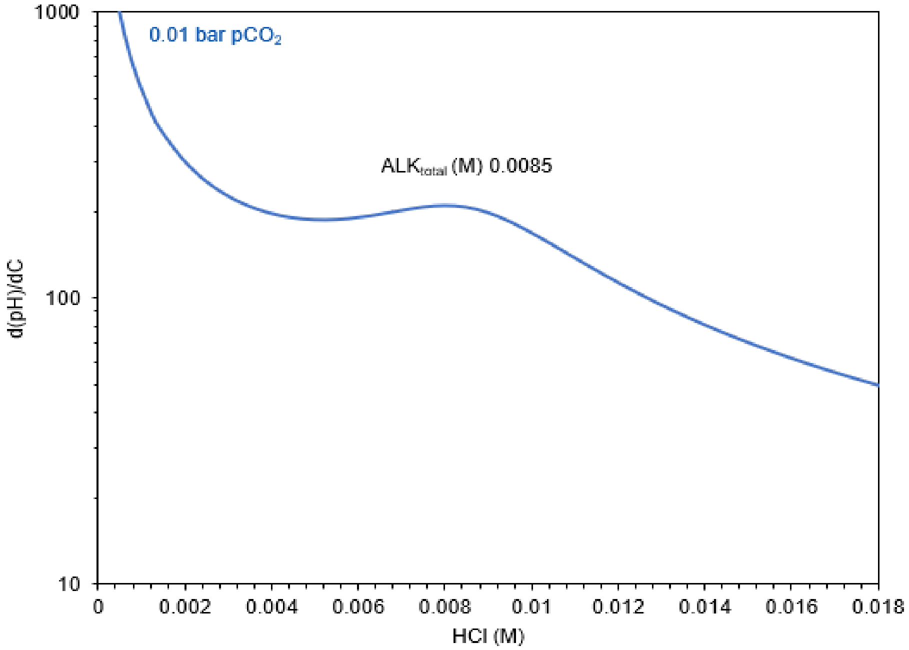


Figure 29: *The d(pH)/d(C) curve for a titration of aqueous sample containing 0.0085 M HCOONa, 0.01 bar* CO_2 *modeled with the modified Rice equation (Figure 28).*

Similarly, the slow titration of a solution consisting of 0.01 M $NaHCO_3$ and 0.0085 M CH_3CH_2COONa with a total alkalinity of 0.0185 M, sparged with 0.01 bar CO_2, is shown in Figure 30. Two separate trials are conducted and compared with the modified Rice equation over the entire pH range. The modeled pH *vs*. $C_{titrant}$ data presents a good match of the total alkalinity, within $\pm 2.0 \times 10^{-4}\ M$ or 1%.

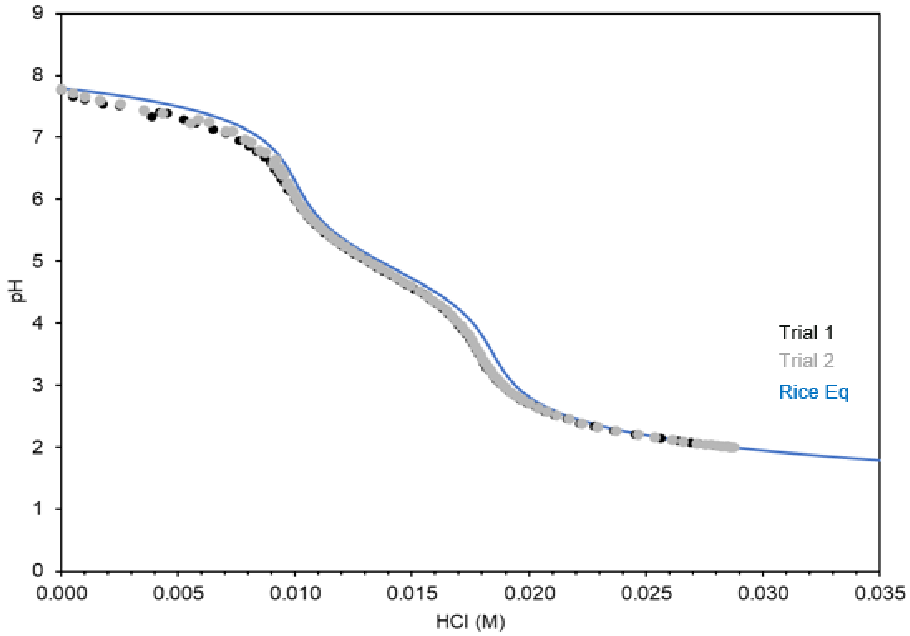


Figure 30: *Aqueous samples of 0.01 M $NaHCO_3$ and 0.0085 M CH_3CH_2COONa, compared to the calculated Rice equation values under constant sparge of 0.01 bar CO_2 (slow titration).*

Finally, the effects of a mixed aqueous solution of carboxylate salts are studied to determine if inflection points from different species would appear on a plot of pH *vs.* $C_{titrant}$ or d(pH)/d(C). A solution consisting of equimolar concentrations of 0.0085 M propionate, acetate, and formate salts is titrated under constant sparge conditions with 0.01 bar CO_2. It should be noted that no $NaHCO_3$ is considered here. Figure 31 shows the results of two separate trials conducted using the slow titration method and compared with modeled data using the modified Rice equation. As expected, there is a good match between experimental and modeled data. However, there is only one visible inflection point on the pH *vs.* $C_{titrant}$ curve, indicating that the contribution to alkalinity due to the different carboxylate salt is indistinguishable. Figure 32 shows the corresponding (pH)/d(C) plot, obtained from modeled modified Rice equation: only one inflection point is distinguishable at the total alkalinity. The fact that the contribution due to acetate and propionate salts cannot be distinguished is fully understandable since they have very close pK_a values. However, the equivalence point corresponding the titration of formate ions should have appeared at a $C_{titrant}$ of 0.017 M. All in all, the pK_a of all these carboxylic acids are still too close to be able to distinguish them on a titration curve.

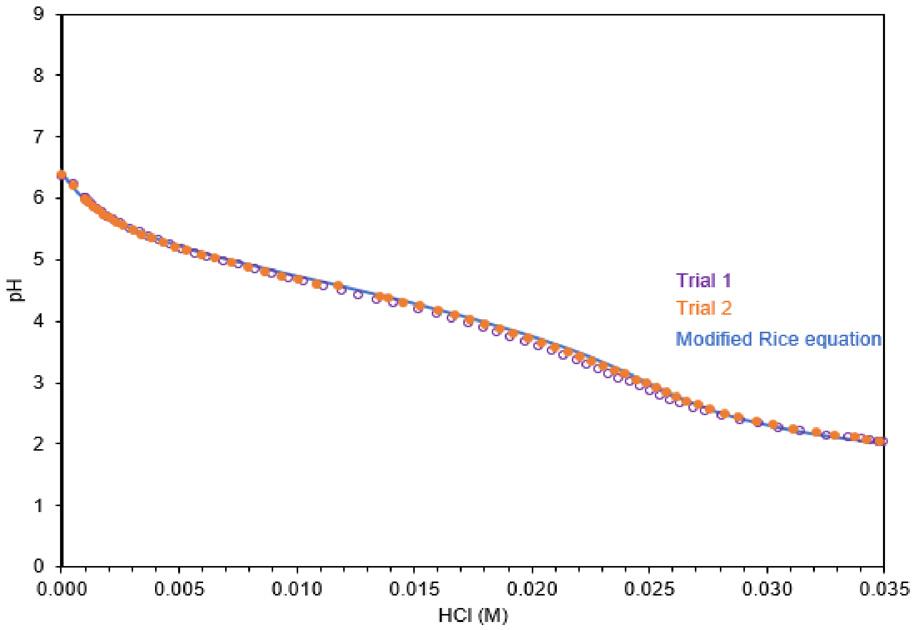


Figure 31: *Aqueous sample made of 0.0085 M sodium propionate, 0.0085 M sodium acetate, and 0.0085 M sodium formate, (for a total alkalinity of 0.255M) compared to the Modified Rice equation under constant sparge of 0.01 bar CO_2 (slow titration).*

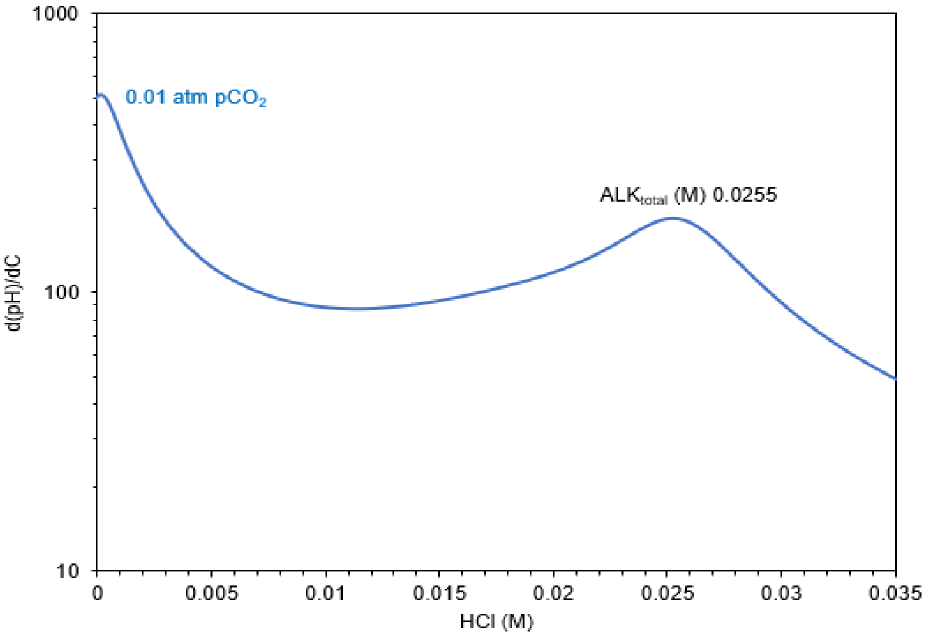


Figure 32: *The d(pH)/d(C) curve for a titration of equimolar concentrations of carboxylate salts, 0.01 bar* CO_2 *modeled with the modified Rice equation (Figure 31).*

6.1.4 Effect of Salt Types and Concentration on Titration of Solutions Containing $NaHCO_3$ and CH_3COONa

Documentation of field water chemistry from industry often report high salt contents and the presence of a variety of salt types. While NaCl is the most dominant salt present, K^+ and Mg^{2+} are also often reported. The presence of salt should have no effect on total alkalinity – yet it can affect the shape of the titration curves and complicate the analysis of the data. In addition, high salt contents generate very non-ideal solutions, therefore modeling requires the use of activity coefficients. The main objective of this section is to document the effect of ionic strength on the titration of solutions containing $NaHCO_3$ and $CH_3COOHNa$.

6.1.4.1 Effect of Ionic Strength on Titrations of Solutions Containing $NaHCO_3$

In this first section, titrations are performed with aqueous solutions containing 0.1 M $NaHCO_3$ and ionic strength ranging from 0.1 to 2 M. The solution ionic strength is adjusted by addition of NaCl. Since no carboxylate salts are added, the solutions are not sparged with CO_2 and titration are performed under atmospheric conditions. All titrations are conducted at least twice and show good repeatability. The solutions are all prepared using the baseline solution of 0.1 M $NaHCO_3$ to which a calculated mass of NaCl is added to reach the desired ionic strength. The total alkalinity of all solutions is constant, at 0.1 M. The results of the titrations are shown in Figure 33. The effect of ionic strength is first visible in the increase in the total alkalinity with increase in ionic strength - the increase is relatively small (around 8%) but noticeable in repeatable trials at 2.0 M ionic strength. This is unexpected since the presence of salt should have no significant effect on alkalinity. It can be also noted that the alkalinity measured at a pH 4.5 endpoint and the alkalinity measured at the equivalence point for the baseline solution (ionic strength of 0.1 M) are exactly the same. At higher ionic strengths, especially at 1.5 and 2.0 M, deviations between the alkalinity values measured at the pH 4.5 endpoint and at the equivalence point are in the 4-8 % range.

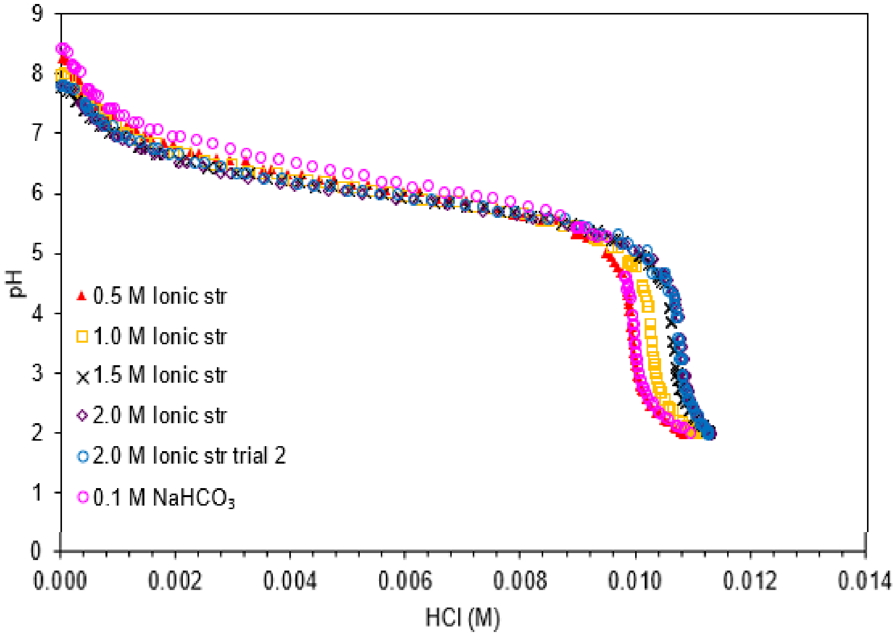


Figure 33: *Titration of an aqueous samples containing NaCl (0.5, 1, 1.5, 2 M) ionic strength, 0.1 M $NaHCO_3$, no gas sparge and atmospheric conditions.*

6.1.4.2 Effect of the Type of Salts on Titrations of Solutions Containing $NaHCO_3$

This next set of experimental titrations are aimed at investigating the effect of the type of salts on the measured alkalinity. Experiments are conducted with a base solution containing 0.1 M $NaHCO_3$ at atmospheric conditions, still without gas sparge. Except for the baseline solution (which holds 0.1 M ionic strength), all other solutions prepared have an ionic strength of 2 M. This is achieved by adding the corresponding mass of NaCl, KCl, and $MgCl_2$, which are all typical of oil and gas production. The experimental titration results are shown in Figure 34. As mentioned in the previous section, the titration of solutions containing 2 M ionic strength presents a total alkalinity 4 to 8% higher than the baseline solution (0.1 M ionic strength). However, the results show that the type of salt added to the brine sample does not have any effect on the measured alkalinity. The deviation between the alkalinity values measured at the pH 4.5 endpoint and at the equivalence point are also the same for all salt types considered. In conclusion, the increase in alkalinity is only due to ionic strength and not the type of salt used.

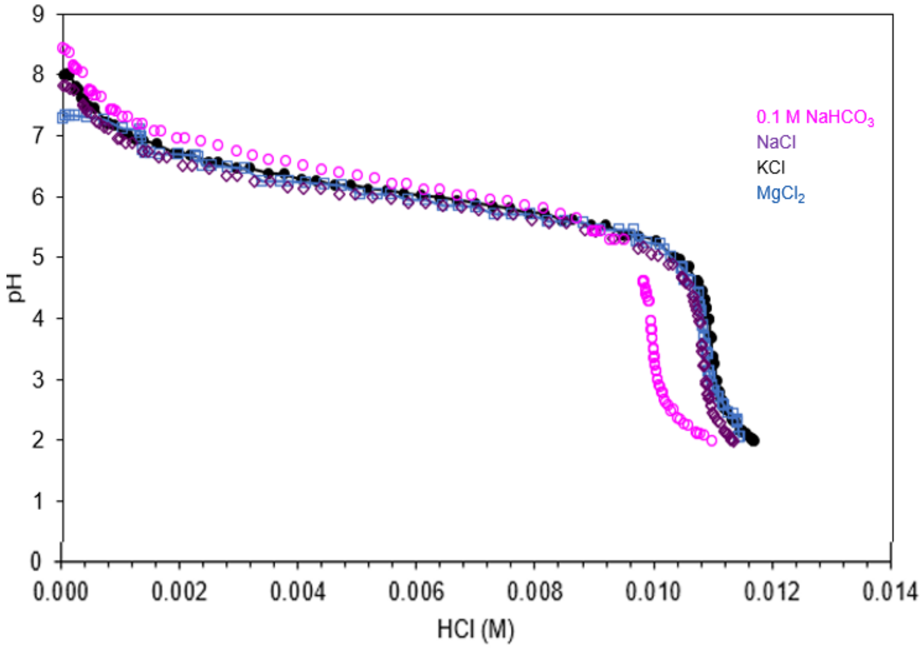


Figure 34: *Titration of an aqueous samples containing different salts at 2.0 M ionic strength, 0.1 M* $NaHCO_3$*, no gas sparge and atmospheric conditions.*

6.1.4.3 Effect of the Ionic Strength on Titrations of Solutions Containing $NaHCO_3$ and CH_3COONa

The next set of experiments incorporates the influence of salts on the titration of solutions containing both $NaHCO_3$ and CH_3COONa. Since acetate salts are present, all experiments are conducted under a CO_2 sparge of 0.01 bar. The base solution is made of 0.01 M $NaHCO_3$ and 0.0085 M CH_3COONa. A calculated mass of NaCl is added to reach the desired ionic strengths, ranging from 0.0185 to 2 M in solution. The baseline solution has a total alkalinity of 0.0185 M. Figure 35 shows the experimental titrations. The effect of increased ionic strengths is mostly seen at the high and low pH ranges – a higher ionic strength decreases the initial equilibrium pH and the final pH when the titration is completed. However, this observation is not relevant when considering the effect on the equivalence points. As discussed earlier, higher ionic strength leads to a marginal increase of the equivalence point associated with the titration of HCO_3^-. The same offset in alkalinity of 4-8 % from the baseline is observed compared to Figure 33. These new results also show that there is a slight effect of ionic strength on the total alkalinity – of the range of 4-5%. Overall, alkalinity is affected minimally by ionic strength.

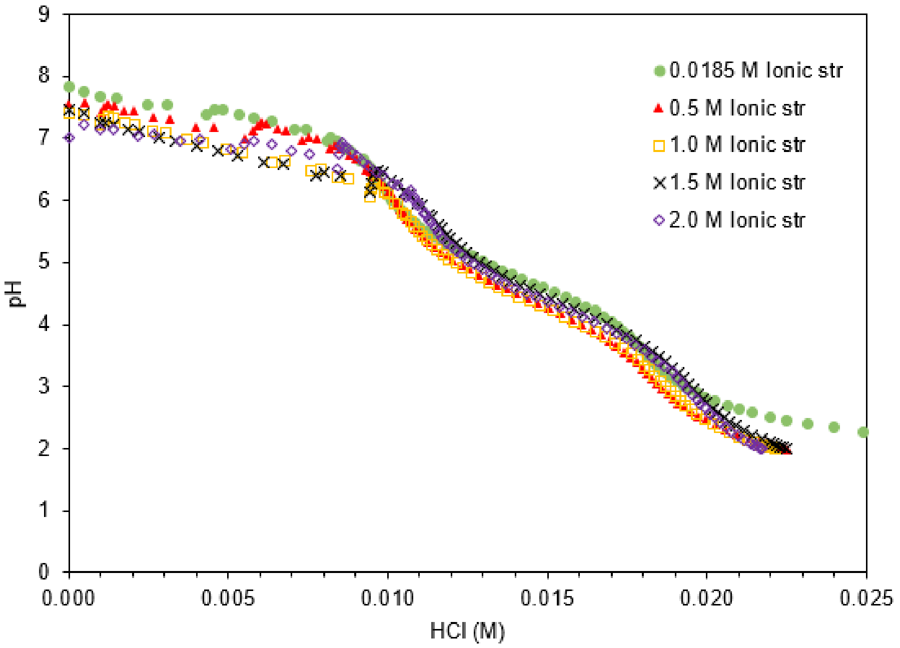


Figure 35: *Titration of an aqueous samples containing NaCl (0.5, 1, 1.5, 2 M) ionic strength, 0.01 M* $NaHCO_3$, *0.0085 M* CH_3COONa, *and 0.01 bar* CO_2 *sparging.*

6.1.4.4 Modeling of Titration Data in Non-Ideal Environments Using the Rice Equation

The use of an activity-based water chemistry model is implemented to model titration data collected at higher ionic strengths. It is important to mention that if activity coefficients are used, any dependance of equilibrium constants listed in Table 4 are removed (*i.e.* ionic strength is set to zero). The Rice methodology does account for non-ideality by the incorporation of activity coefficients in the main equation. Generating activity coefficients is done using the OLI® Mixed Solvent Electrolyte (MSE model) [16]. A short high-level description of this model is shown in Appendix 9.1. The values of activity coefficients change as the titrations are being performed since large changes in H^+ concentration is experienced. Ideally, the titration model should be linked to a non-ideal water chemistry model capable of generating updated activity coefficients corresponding to each incremental change in pH. This effort is outside the scope of this study. Instead, the entire pH scale of the titrations was divided into three ranges: (initial pH – pH 4.5), (pH 4.49 – pH 3), and (pH 2.99 – final pH). Activity coefficients were obtained using 7.7 pH representing the equilibrium pH with no H^+ added, 4.0 pH representing the 0.015 M H^+ added, and 2.5 pH representing 0.02 M H^+ added. The activity coefficients for each pH were assumed constant for the range of pH values. It is understood this is not an ideal approach, but it still constitutes an acceptable first step. The choice of pH ranges was done to match the pH range of the equivalence points corresponding to $NaHCO_3$ and CH_3COONa. The full list of values can be found in Table 13-Table 15 of the Appendix 9.1.The effect of ionic strength on modeled titration data, that include activity coefficients, is shown in Figure 36.

The base line solution is chosen as containing 0.01 M $NaHCO_3$ and 0.0085 M CH_3COONa. The added salt species is simulated as NaCl and ionic strengths of 0.0185, 0.5, 1, 1.5, 2 M are considered. The main influence of increased non-ideality (increased ionic strength) is seen in the decrease of the initial pH. The decreases in the initial pH is caused by the increase in the $\frac{fHCO3K_{ca}K_{sol}K_{hy}\,P_{CO_2}\,\lambda_{CO_2}}{10^{-pH}\lambda_{HCO_3^-}}$ term in the Rice equation (Equation 6). The increase is caused by the ratio of activity coefficients $\frac{\lambda_{CO_2}}{\lambda_{HCO_3^-}}$ increasing with greater ionic strength. The influence of activity coefficients on the acetate term is not as pronounced, but the $\frac{TAc^-}{\frac{10^{-pH}\lambda_{Ac}^-}{fAc*K_{HAc}\lambda_{HAc,eq}}+1}$ term increases with increasing ionic strength, as the $\frac{\lambda_{Ac^-}}{\lambda_{HAc,eq}}$ ratio decreases. Overall, the modeled titrations, taking a full account of non-ideality, do not show a significant influence of ionic strength on equivalence points and total alkalinity. The same observation was done earlier on experimental titrations.

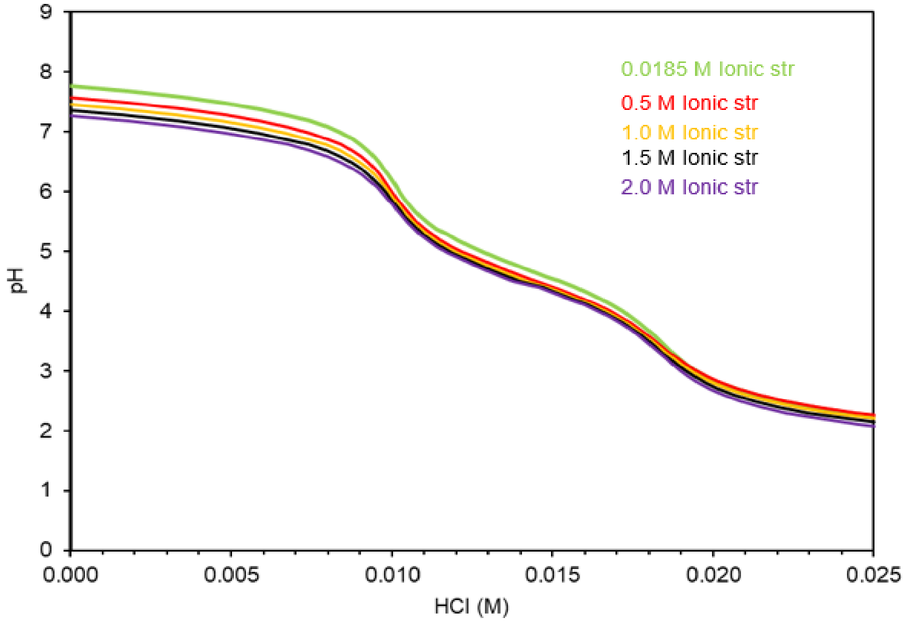


Figure 36: *Modeled titration curves using the Rice equation with activities coefficients of samples containing NaCl (0.5, 1, 1.5, 2 M) ionic strength, 0.01 M* $NaHCO_3$*, 0.0085 M* CH_3COONa*, and 0.01 bar of* CO_2*.*

Experimental and modeled titrations are then compared for 0.5- 2 M ionic strength in Figure 37, Figure 38, Figure 39, and Figure 40, respectively. Similar comments can be made for all comparisons. In the presence of salts, the match between experimental and modeled data is not as good as in ideal solutions. The largest discrepancy occurs below pH 2.5. Fortunately, this pH range is of little interest for the titrations. The observation was made that a “bump” appeared near pH 7 in titrations carried out in non-ideal conditions with salt. This “bump” is suspected to be from an error in the measurement of pH caused by a synergistic affect between high salt environments and a neutral pH in solution. There is a reasonable match in the high pH and some relatively small discrepancies can be seen at the HCO_3^- equivalence point and the total alkalinity. However, the deviation never exceeds more that 5%.

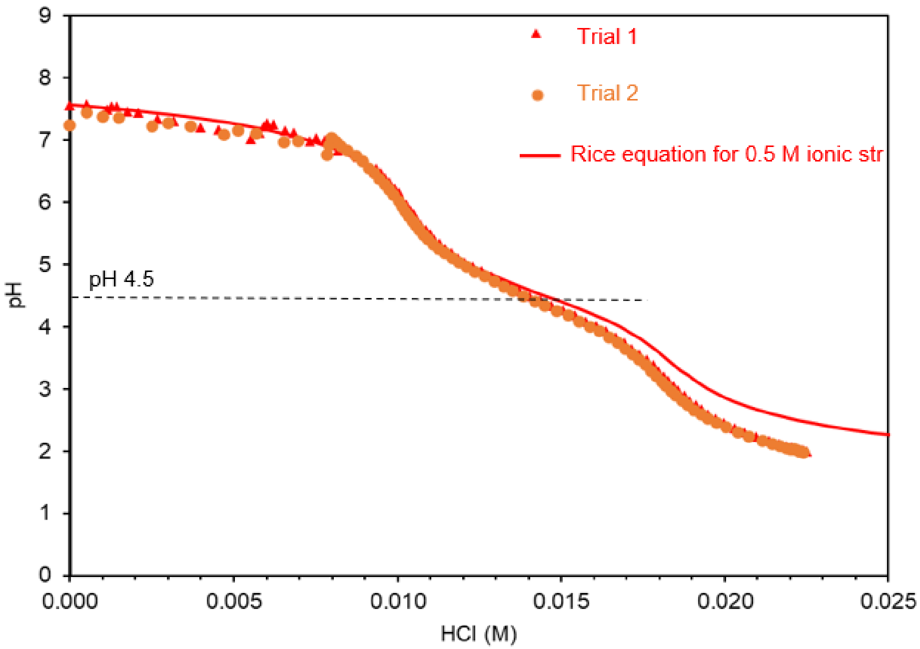


Figure 37: *Titration of an aqueous samples containing 0.5 M NaCl ionic strength, 0.01 M* $NaHCO_3$*, 0.0085 M* CH_3COONa*, and 0.01 bar of* CO_2 *compared to the Rice equation accounting for activity coefficients.*

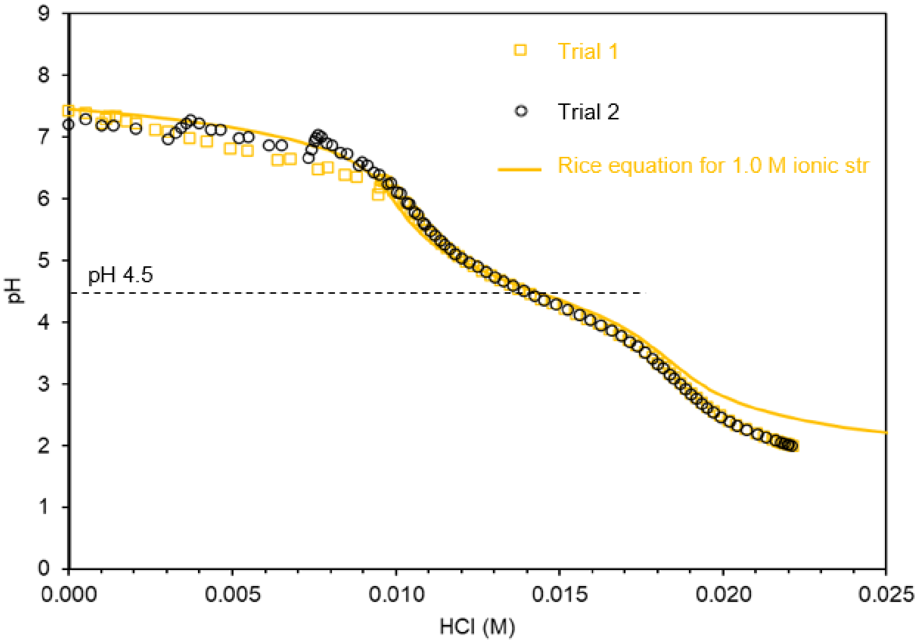


Figure 38: *Titration of an aqueous samples containing 1.0 M NaCl ionic strength, 0.01 M* $NaHCO_3$*, 0.0085 M* CH_3COONa*, and 0.01 bar of* CO_2 *compared to the Rice equation accounting for activity coefficients.*

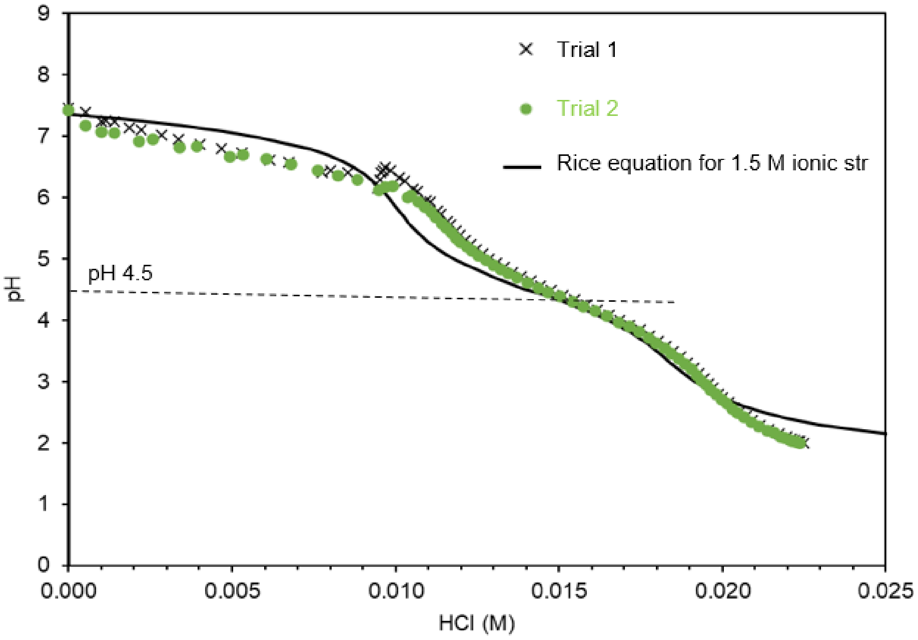


Figure 39: *Titration of an aqueous samples containing 1.5 M NaCl ionic strength, 0.01 M* $NaHCO_3$*, 0.0085 M* CH_3COONa*, and 0.01 bar of* CO_2 *compared to the Rice equation accounting for activity coefficients.*

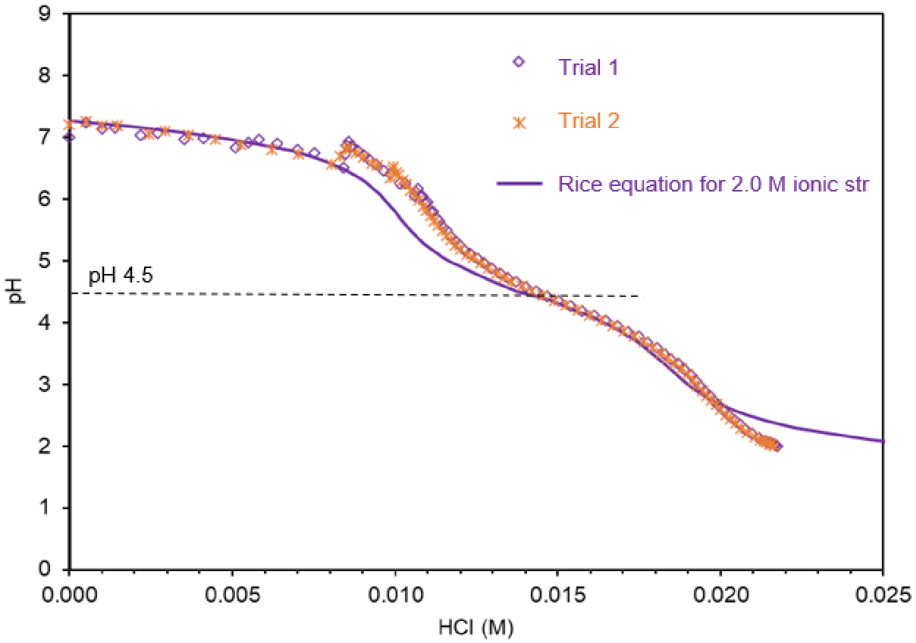


Figure 40: *Titration of an aqueous samples containing 2.0 M NaCl ionic strength, 0.01 M* $NaHCO_3$*, 0.0085 M* CH_3COONa*, and 0.01 bar of* CO_2 *compared to the Rice equation accounting for activity coefficients.*

6.2 Lessons Learned from Review of Experimental Titrations

The review of the experimental work presented in the previous section can yield useful information on how to best perform titrations in the laboratory. While the Rice methodology is indeed very appropriate, several procedural aspects are discussed in this section to clarify their purpose and consequences on the validity of the collected data. Two main aspects of the methodology are discussed here: the titration speed and the use of CO_2 sparging during and prior to titrations. The necessary time to reach equilibrium in water samples was also reviewed to ensure equilibrium conditions are met prior to conducting titrations.

6.2.1 Comments on the Effect of CO_2 Sparging

Prior to each titration involving CO_2 sparging, it is important to ensure that liquid/gas equilibrium is reached. Some short experiments are carried out to document the time required to reach equilibrium. Five different 100 ml sample with a concentration of 0.01 M $NaHCO_3$ and 0.0085 M CH_3COONa are prepared for samples. The solution pH is recorded as the CO_2 sparge starts. The effect of five different sparging partial pressures of CO_2 are considered, the completing gas being N_2. The literature available indicated a sparge of 20-30 min was adequate to achieve equilibrium at a flow rate of 1 L/min [26] [28]. Experimental results, shown in Figure 41, confirm that equilibrium can be reached within 15 min with a flow rate of 1 L/min. Equilibrium conditions are reached when there is no recorded change in pH with time (d(pH)/d(t) approaches zero). The use of CO_2 sparging changes the initial pH, increasing the CO_2 partial pressure decreases the initial pH of the sample. Initial pH values vary from 5.88 at 1 bar to 8.07 pH at 0.0063 bar pCO_2. Discrepancies in the initial pH are due to timing of when measurements were taken and when data collection began.

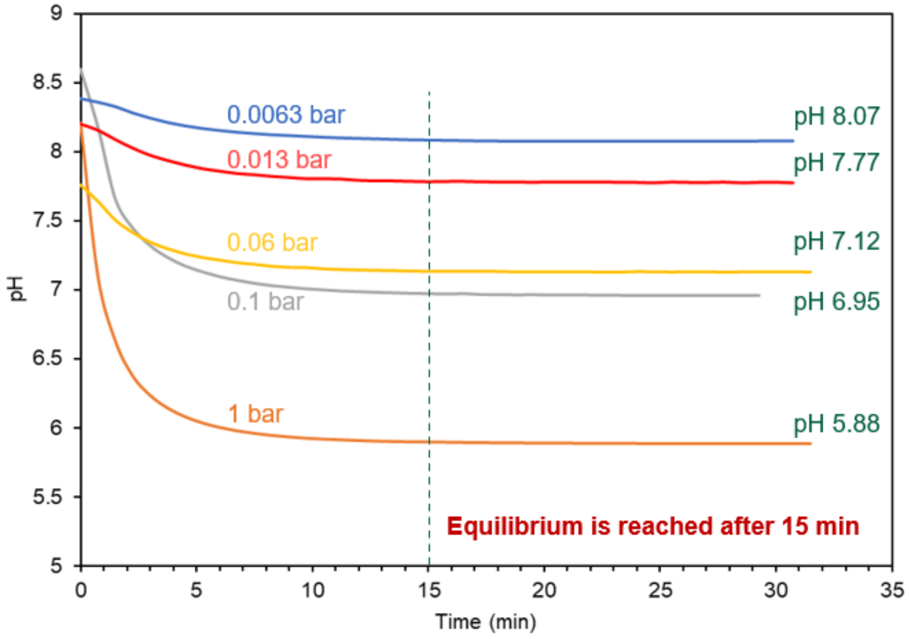


Figure 41: *pH vs time data for a 100 ml aqueous sample containing 0.01 M* $NaHCO_3$*, and 0.0085 M* CH_3COONa *under constant sparge (1-0.0063* pCO_2*).*

The use of CO_2 sparging gives insight into the chemical composition of a sample (*i.e*. whether or not carboxylate salts are present). The Rice equation can model titrations with active CO_2 sparge while the Henderson equation is applicable for titrations in atmospheric environments without active sparge. The Henderson methodology/equation implies that the sample is not at equilibrium with the atmosphere once titrant is added and the equilibriums is disturbed. The effect of CO_2 sparging *vs*. no gas sparging on titration data are shown in a direct comparison in Figure 42. The CO_2 sparge (with 0.01 bar CO_2) sets a lower initial pH and maintains the equilibrium while the titrant is added. The equilibrium that is maintained during sparging acts as a buffering effect that resists changes in pH, whereas in the sample that is not sparged there is a rapid drop in pH initially then a gradual slope to the equivalence point. The shaded region from the initial pH to approximately pH 5.3 remains the only difference when comparing collected titration data with or without CO_2 sparge.

The experimental data points are compared with the Rice equation or the Henderson equation. Typically, no fitting (*i.e.*, regression on correcting factors) is required when using known/simple solutions. Plots of d(pH)/d(C) are extracted from either the Henderson or the Rice equation to better visualize different end points (*i.e.*, different contributions to alkalinity). It is clear that contributions to alkalinity from bicarbonate species and carboxylate species can be more easily separated when samples are under CO_2 sparge. Yet, both methods would determine the same total in the solution.

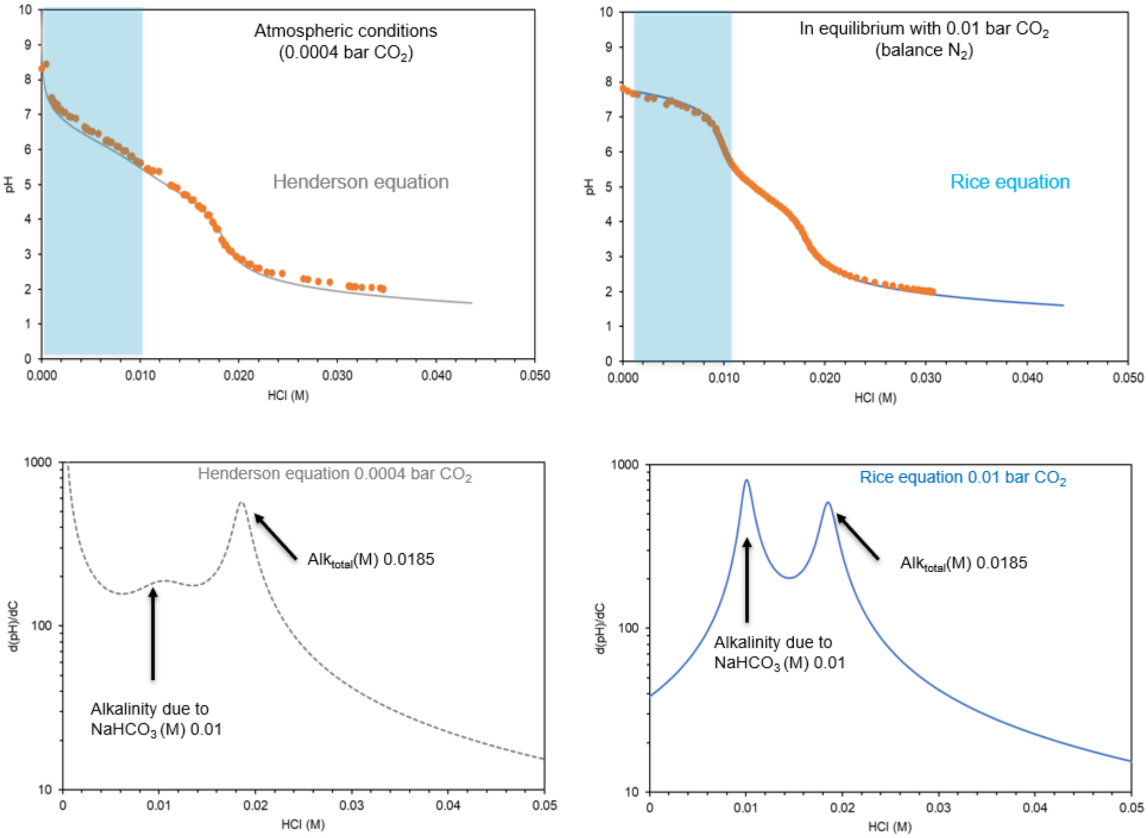


Figure 42: *Effects of bubbling and analysis of titration data from a known brine (100 ml): 0.01 M $NaHCO_3$ and 0.0085 M CH_3COONa, with and without 0.01 bar P_{CO2} [34].*

The use of CO_2 sparging maintains equilibrium in the aqueous sample with the set CO_2 partial pressure. The alkalinity is a conserved parameter and does not change regardless of the thermodynamic conditions, temperature, and partial pressure. In other words, water chemistry species (OH^-, H^+, CO_3^{2-}, HCO_3^-) are converted to reflect the thermodynamic conditions, the cation concentration remains the same. Figure 43 shows an example of a sample containing 0.01 M NaOH and 0.0085 M CH_3COONa with and without active CO_2 sparge with 0.06 bar CO_2. In this example, the weak base that is typically added to the aqueous sample ($NaHCO_3$) is replaced by a strong base (NaOH). The titration conducted at atmospheric conditions, without CO_2 sparging, displays characteristics of a strong base containing OH^- (at least until the first inflection point), whereas the sample that was CO_2 sparged still contains the same value of alkalinity but has properties of a weak base strong acid titration. The species contributing to the value of alkalinity in the sparged condition are HCO_3^- and Ac^-. This furthers the point that alkalinity can be in the form of many different species, it is not just about HCO_3^- concentration.

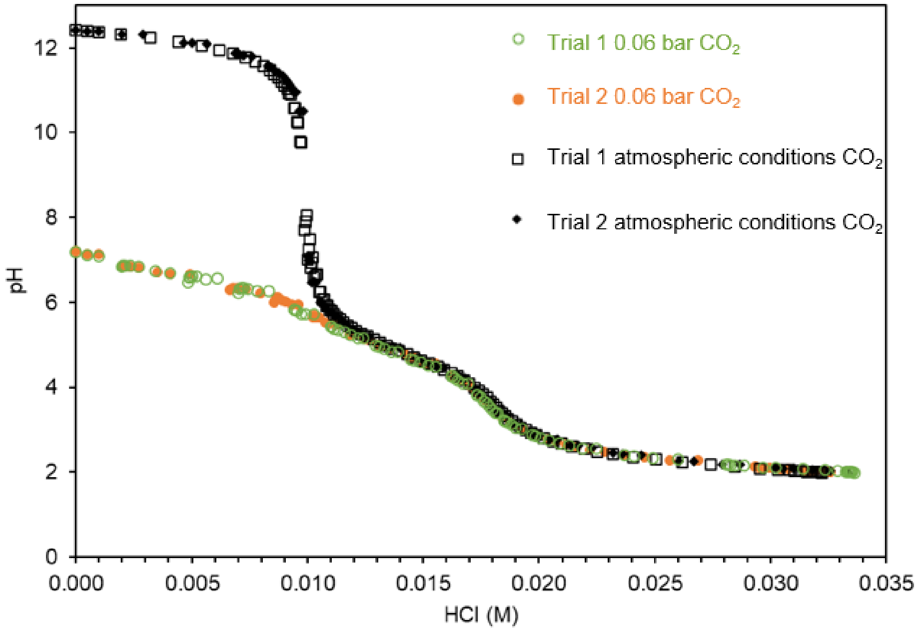


Figure 43: *Titration of an aqueous samples containing 0.01 M NaOH, 0.0085 M* CH_3COONa*, with and without a 0.06 bar* CO_2 *sparge.*

6.2.2 Comment on the Effect of Sampling Rate

When a CO_2 sparge is used, the rate at which the titrator collects data (*i.e.* rate at with titrant is added) affects the equilibrium of each point in the titration curve. There is no need for long wait times when sparging is not used, *i.e.*, the Henderson methodology. A wait time of 10-20 sec between titrant additions is sufficient. However, when CO_2

sparge is used, slower titration speed can be required to allow for the CO_2 equilibrium to be established. As mentioned earlier, on the benefits of CO_2 sparging and the Rice methodology as a whole is to identify clearly the presence of carboxylate salts and their contribution to the total alkalinity. Not setting a long enough delay between titrant additions in order to attain equilibria with the added titrant can lead to collection of data in non-equilibrium states, halfway between the Rice and the Henderson methodology. Testing shows that a titrant addition rate of 1.8 ml/hr with a gas flow rate of 1 L/min is needed at $pCO_2 \leq 0.01$ bar. This is also confirmed by publication describing the Rice methodology [28].

The titrator is set to use a signal stability mode in which the instrument waits a specific time interval set by the user (Δt) during which the potential measured by the pH probe (mV) must become stable ($\Delta E/sec \leq 4$ mV). The new signal value is acquired if the stability condition set by the user is reached after the minimum wait time (t_{min}). If the stability condition is not reached and the maximum wait time (t_{max}) has elapsed, the potential is taken anyway. Signal stability mode allows for large additions of titrant in the buffering region of the curve and smaller additions near the equivalence point. The signal stability mode is referred to as a fast titration mode. The fast titration mode is recommended to be used with the Henderson equation and can be used with the Rice equation at higher partial pressure sparges ($pCO_2 > 0.01$ bar). If titration data is collected too quickly under the signal stability mode, the solution will not have a chance to reach equilibrium at the constant sparge conditions. The titration data will then not be taken at equilibrium and will fall below the modelled Rice equation, more closely resembling the modelled Henderson equation (Figure 44). The Henderson methodology is much faster and able to account for titration data near the equivalence point however, the method does not include a defined technique to detect the presence of carboxylates in the sample.

The titrator can also be programmed to what is referred to as a slow titration method. The slow titration method sets the titrator to do the same stability mode but only adds titrant every 60 seconds. The time to carry out titrations intended to be used with the Rice methodology has already been described as a disadvantage. Figure 4, is an example of a slow titration conducted with this method under constant sparge.

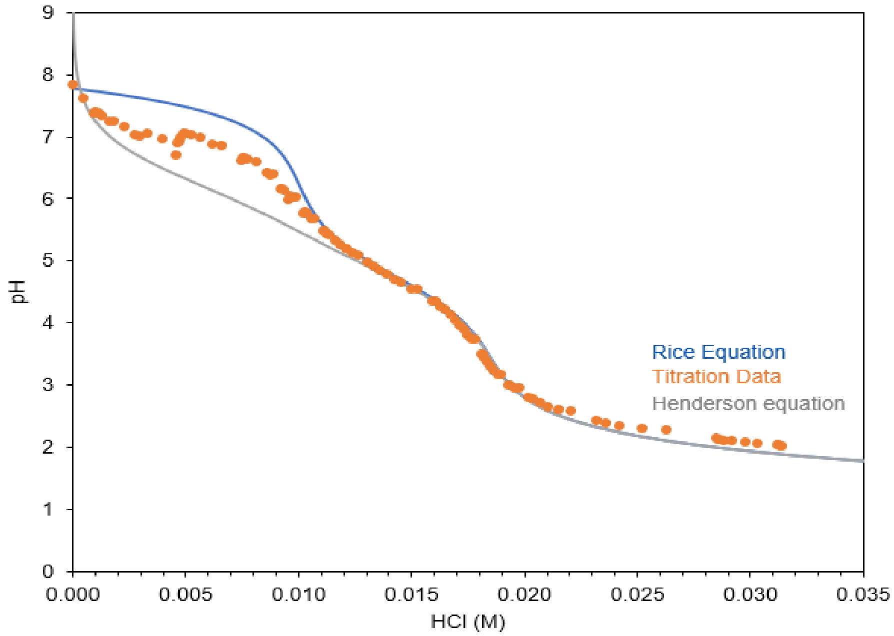


Figure 44: *Aqueous sample of 0.01 M* $NaHCO_3$ *and 0.0085 M* CH_3COONa*, where the titrant was added too quickly under constant sparge 0.01 bar* CO_2*.*

6.2.3 Comments on Modeling Titration Data Using the Rice or Henderson Equation

The specificities of the Rice and Henderson methodologies are discussed in the previous sections. The similarities between the two methods are such they both effectively calculate the total alkalinity at the equivalence point in titrated water samples. As shown in Figure 44, the data modeled with either model converge at a pH value approximately below 5. This holds true for a variety of different concentrations. The differences between the two methods have been discussed at length already – CO_2 sparging is required for the Rice methodology, whereas it is not for the Henderson methodology. The sampling rate can be much faster (fast titrations with titrant additions between 2 to 20 seconds.) when the Henderson equation is used to model titration data, while the Rice methodology is more time intensive, since it may involve slow titrations. If the total alkalinity is the only parameter of interest, then the Henderson equation titrated to the true equivalence point works fine. The advantage of the Rice equation is its ability to identify the presence of carboxylate salts and their contribution to the total alkalinity.

The parameters included in the Rice equation all influence the shape of the Rice titration curve in different ways. The major variables that influence titration data collected using the Rice equation methodology are pCO_2, ionic strength, and activities. The initial pH region of the curve is influenced by pCO_2, $\gamma_{HCO_3^-}$, γ_{CO_2}, and ionic strength. An increase in pCO_2 and $\gamma_{HCO_3^-}$ causes is decrease in the initial pH of titration data. An increase in γ_{CO_2}, and ionic strength cause a decrease in the initial pH of titration data. The influence of TAc^- (total carboxylate) causes a shift in the titration data to higher values of pH, causing a higher value of alkalinity to be measured as carboxylate salts concentration increases, and creates additional peaks detectable on plots of d(pH)/d(C). The activities of organic acid γ_{HAc} and γ_{Ac^-} influence the central region 5.3-4 pH. The primary influence at the low pH values is γ_{H^+}, the activity coefficient for the hydronium ion. A guide of areas of the curve influenced by changing different parameters in the Rice equation is shown in Figure 45.

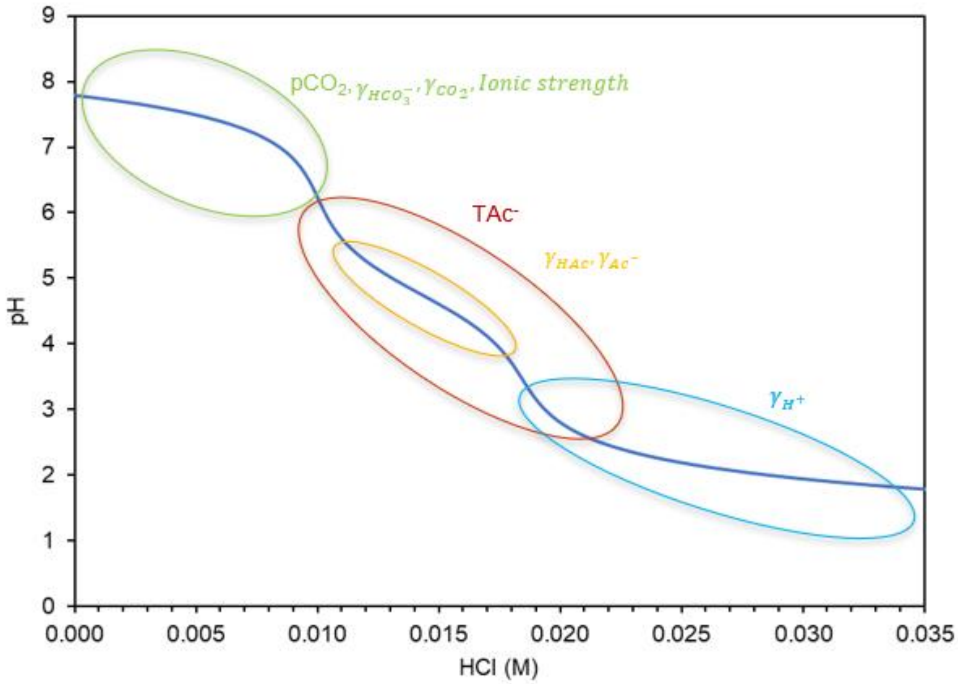


Figure 45: *Influence of operating variables as they apply to the Rice equation curve. Aqueous sample of 0.01 M* $NaHCO_3$ *and 0.0085 M* CH_3COONa*, under constant sparge 0.01 bar* CO_2

6.3 Application of the Rice Methodology to the Analysis of Field Brine Samples

Two field brines with corresponding chemical analysis were titrated in the laboratory following the Rice methodology. The objective of this section was to evaluate if the total alkalinity and the presence of carboxylate salts can be correctly identified in an unknown brine.

The composition of the first field brine is described in Table 9. As expected, several pieces of information lack clarity. The temperature and initial pH of the solution are not given in the original analyses. The assumption must be made that the measurement was conducted at 25°C in lab conditions. The total alkalinity is reported as ppm$_w$ HCO_3^- and the organic acid content is also reported. Yet there is not information on how the alkalinity was determined.

Table 9: *Brine analysis report #1 listing the concentrations of cations and anions (ppm) present in an unknown water chemistry sample.*

Parameters	**Units**	**Field Brine #1**
Density @ 25°C	g/cm^3	-
Conductivity	mS/cm	-
Alkalinity as HCO_3^-	mg/L	137
TDS	mg/L	-
Na^+	mg/L	29828.6
K^+	mg/L	1437
Mg^{2+}	mg/L	2321
Ca^{2+}	mg/L	17770
Cl^-	mg/L	85092
SO_4^{2-}	mg/L	440
Organic acid	mg/L	30

The alkalinity can also be calculated by the molar balance of cations and anions of salts in solution (Equation 4), although these rarely work out correctly when concentrations are taken directly from a water chemistry analysis. When the molar balance of cations and anions are considered for this unknown brine, the alkalinity would be 0.00325 M (198 ppm$_w$ HCO_3^-), corresponding to an error of 45%. However, as discussed earlier, there are far too many uncertainties in the given cation and anion concentrations to calculate alkalinity accurately using this method. However, checking the molar balance of cations and anions is helpful in determining the accuracy of the provided data. If available, data obtained from a pH titration always provides the best accuracy.

The intended outcome is to compare the calculated value of total alkalinity listed in a water chemistry analysis report to the measured alkalinity found in the lab by pH titration. The brine is titrated using a 0.01 bar CO_2 sparge, using a slow titration, and fitted with modeled data using the Rice equation (Equation 6). The d(pH)/d(C) collected using the Rice methodology on Brine #1 can be found in Figure 47. The initial lack of data points is caused by the titrator making a dose which was too large for the buffering of the solution. The paired data points are seen when very small addition volumes stick to the tip of the titrator before a drop is large enough to fall.

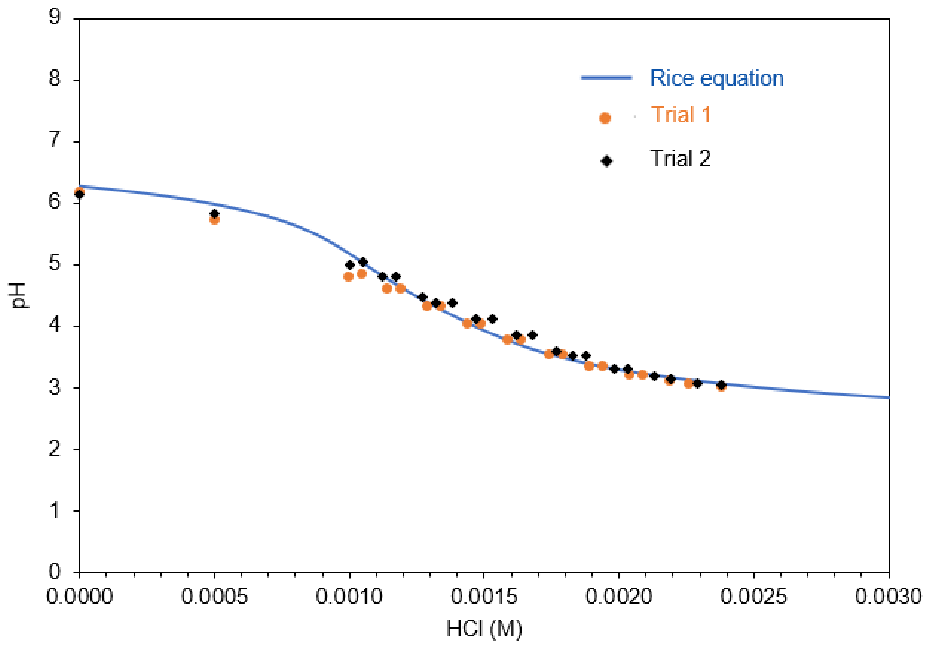


Figure 46: *Brine #1 titration data with a total alkalinity of 0.0015 M fitted with the Rice equation under constant sparge of 0.01 bar* CO_2*.*

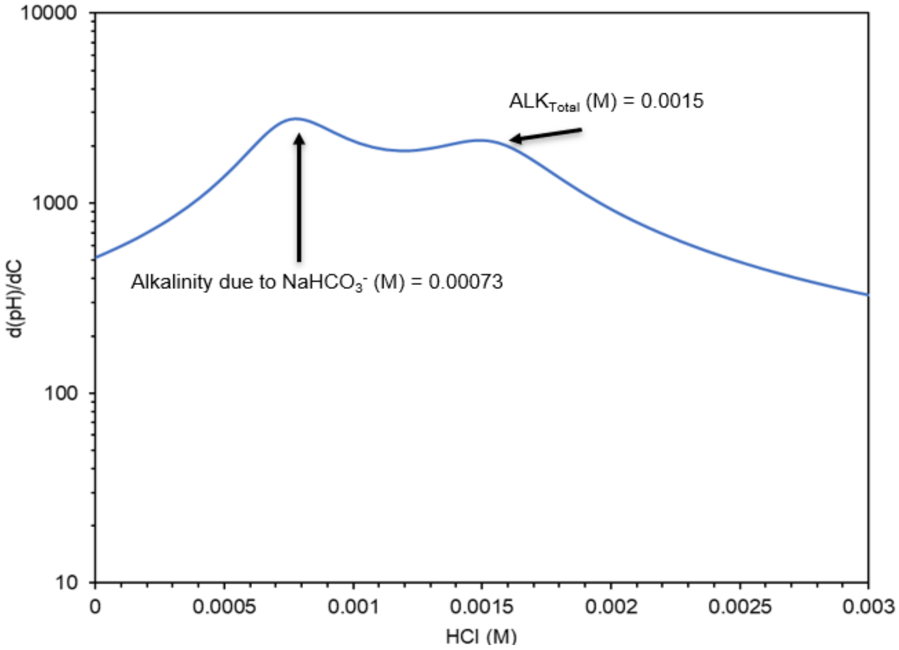


Figure 47: *The d(pH)/d(C) curve for titration data with a total alkalinity of 0.0015 M fitted with the Rice equation under constant sparge of 0.01 bar* CO_2

The correction factors $fHCO_3^-$, fAc^- are assumed to be unity. The values for the activities were taken from of Table 13-Table 15 of Appendix 9.1 for an ionic strength of 2 M. The only fitted parameters are “Alk” (total alkalinity), as TAc^- (total acetate concentration) is given in the water chemistry analysis. The use of an activity-based model is not really needed when only fitting the total alkalinity but was used for completeness. The total alkalinity of the brine is measured to be $0.00151 \pm 0.00004\ M$ or 2% considering the error between the two trials when only fitting “Alk” (total alkalinity). When both “Alk” and TAc^- are fitted, the total alkalinity of the brine is measured to be $0.00153 \pm 0.00004\ M$ or 2%. If the carboxylate salts concentration is given in the brine analysis document it should be used directly, limiting the error associated with performing nonlinear regression on more than one variable. The alkalinity value using the balance of cations and anions of salts is calculated to be 0.00325 M – this is inherently inaccurate and can be discarded outright. The water chemistry also lists an alkalinity value in terms of ppm$_w$ HCO_3^- which, if converted to molar, corresponds to 0.00225 M. The values obtained from these three methods can be found in Table 10. The difference between the laboratory measured value and what is reported in the analysis is considerable. The discrepancy could come from difficulties in accuracy of the field brines in the lab. Most likely, errors in reporting are to be blamed. It is interesting to notice that if an endpoint titration at pH 4.5 had been performed, the measured alkalinity would have been even lower. It is also possible that the discrepancies between the measured alkalinity value from experimental titration and the alkalinity listed on the water chemistry could be explained by mislabeling the alkalinity as ppm$_w$ HCO_3^- instead of ppm$_w$ $CaCO_3$, but this is a very unlikely scenario. If the given alkalinity is assumed to have units of ppm$_w$ $CaCO_3$, then conversion to molar units would give 0.0014 M, which would agree well with the measured alkalinity value from titration.

Table 10*: Measured and calculated values of total alkalinity and organic acid from brine #1 analysis.*

Test	Concentration
Alkalinity from titration	$\mathbf{Alk_{total}\,(M) = 0.0015 \pm 0.00004}$
Alkalinity from the water chemistry documentation (137 ppm$_w$ HCO_3^-)	$\mathbf{Alk_{total}\,(M) = 0.00225}$
Alkalinity based on salt cation/anion balance	$\mathbf{Alk_{total}\,(M) = 0.00325}$
Organic acid concentration from documentation (30 ppm$_w$ organic acid)	$\boldsymbol{Ac^-(M) = 0.00051}$

A second brine listed in Table 11 was studied with a higher alkalinity value listed on the water chemistry analysis. The same shortcomings associated with the reporting of the first brine are true here as well.

Table 11: *Brine analysis report #2 listing the concentrations of cations and anions (ppm_w) present in an unknown water chemistry sample.*

List of tests	**Unit**	**Field Brine #2**
Density @ 25 ◦C	g/cm^3	-
Conductivity	mS/cm	-
Alkalinity as HCO_3^-	mg/L	239
TDS	mg/L	-
Na^+	mg/L	16366.3
K^+	mg/L	1898
Mg^{2+}	mg/L	1453
Ca^{2+}	mg/L	8244
Cl^-	mg/L	45113
SO_4^{2-}	mg/L	712
Organic Acid	mg/L	70

The brine was titrated using a 0.01 bar CO_2 sparge, slow titration, and fitted using the Rice equation (Equation 6). The correction factors $fHCO_3^-$, fAc^-, are assumed to be one. The values for activities are taken from Table 13-Table 15 of the appendix for an ionic strength of 1.5 M. The only modified parameter for fitting is “Alk” (the total alkalinity), as TAc^- (the total acetate concentration) is given in the water chemistry analysis.

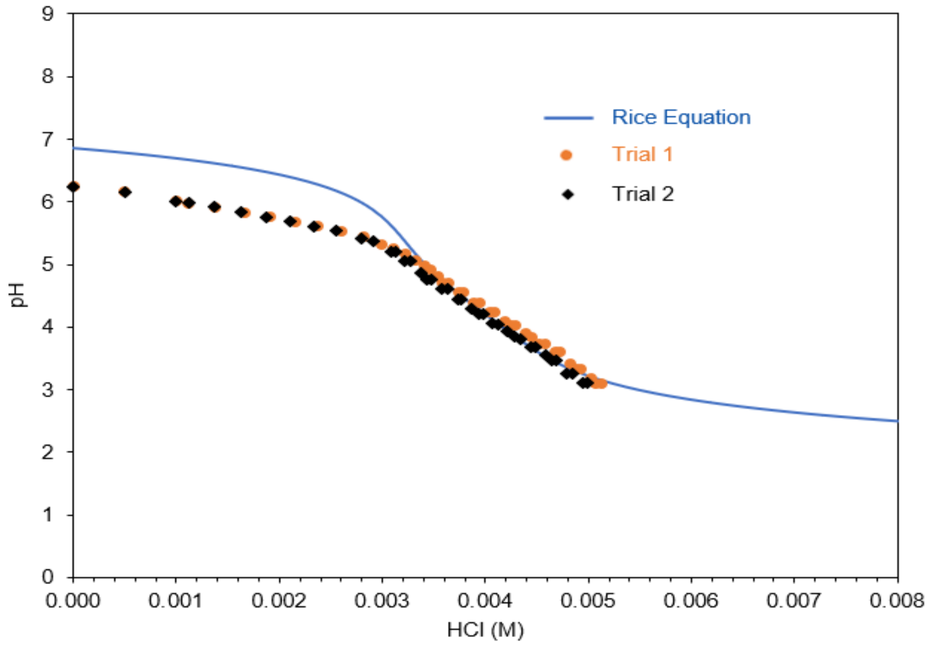


Figure 48: *Brine #2 titration curve with a total alkalinity of 0.0044 M fitted with the Rice equation under constant sparge of 0.01 bar* CO_2.

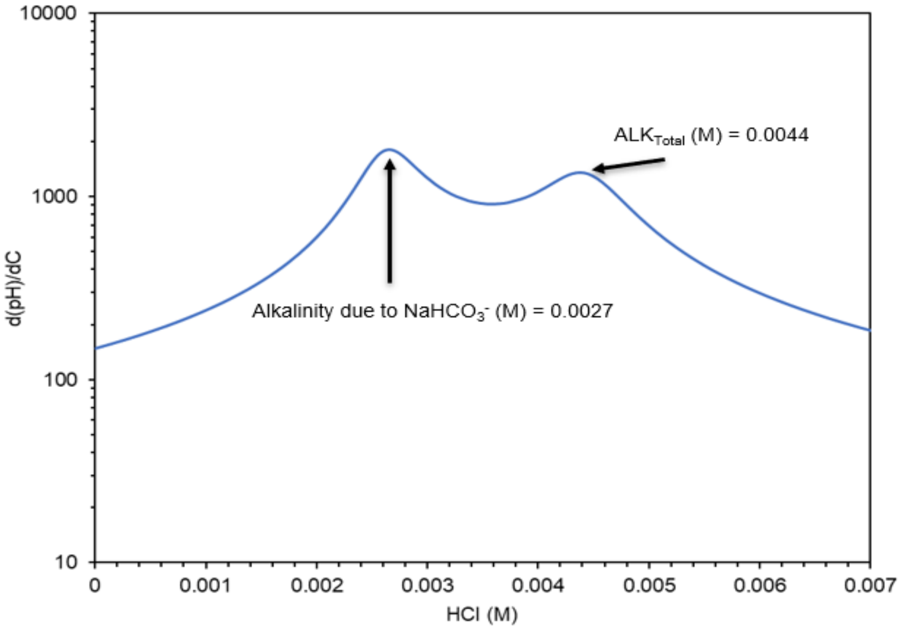


Figure 49: *The d(pH)/d(C) curve for titration data with a total alkalinity of 0.0044 M fitted with the Rice equation under constant sparge of 0.01 bar* CO_2

The overall fit of the Rice method is poor at higher pH values, where HCO_3^- activity coefficients influence the curve - errors in activity coefficients could contribute to an inadequate fit. However, the region near the equivalence point gives a good fit for measuring the total alkalinity. The total alkalinity of the brine is measured at $0.0044 \pm 0.00008\ M$ or 2% when only fitting "Alk" (total alkalinity). When both "Alk" and TAc^- were fitted the total alkalinity of the brine is measured to be $0.0043 \pm 0.00004\ M$ or 1%. The alkalinity value using the balance of cations and anions of salts is calculated to be 0.00442 M. The water chemistry also lists an alkalinity value in terms of ppm_w HCO_3^- which, if converted to molar, corresponds to 0.0039 M. The values obtained from these three methods can be found in Table 12. Comparing the errors to the total alkalinity using the Rice equation, the cation anion balance gives, somehow surprisingly, 4.5% difference where the total alkalinity listed on the water chemistry differs by 11%. The calculated value based on the salt balance along with the alkalinity value listed on the water chemistry agree well with the titrated value.

Table 12: *Measured and calculated values of total alkalinity and organic acid from brine #2.*

Test	**Concentration**
Alkalinity from titration	$\mathbf{Alk_{total}\ (M) = 0.00438 \pm 0.00008}$
Alkalinity from the water chemistry documentation (239 ppm_w HCO_3^-)	$\mathbf{Alk_{total}\ (M) = 0.00391}$
Alkalinity based on salt cation/anion balance	$\mathbf{Alk_{Total}\ (M) = 0.00442}$
Organic acid concentration from documentation (70 ppm_w organic acid)	$\boldsymbol{Ac^-(M) = 0.00118}$

6.4 Recommendations

The collection of accurate and useful titration data can be done either by the Henderson or Rice methodology (*i.e.* either with or without CO_2 sparge). Recommendations when using either of these methods are as follows:

- The methods require the titration sample to be at room temperature with no solid precipitates. Solid precipitates present in the sample will cause an error in the measurement of alkalinity.
- For the highest accuracy, titrations should be conducted with a potentiometric titrator that has a set endpoint of pH 2. This will avoid missing the location of the equivalence point that would otherwise not be visible if titrations were conducted to pH 4.5.
- Data collected using either the Henderson or Rice titration methodologies should be modeled using the corresponding method. The compared model should then be analyzed using a $d(pH)/d(C_{titrant})$ and the equivalence point recorded on water chemistry documentation.
- The Henderson and Rice equation methods both give the same value of total alkalinity, with the primary difference being that a CO_2 sparge is required for use of the Rice methodology.
- The partial pressure of 0.01 bar CO_2 is recommended to be used as the sparge gas. It is understood that it is not feasible to conduct full titrations on every water sample from industry.

- The Henderson equation is recommended to be used where the total alkalinity is the only value of interest. This also assumes that the organic acid concentration is collected using other chemical analysis for corrosion estimation and included in the water chemistry. The titration can be conducted with a fast titration and the equivalence point extracted with a d(pH)/d(C) from the modeled curve.
- The Rice method is recommended to be used if the organic acid concentration is not measured from other methods or if confirmation on the amount of organic acid is desired. There is no need to take the time to conduct a slow titration with the Rice equation if the total alkalinity is the only value of interest.

Several recommendations involving water chemistry documents can be made to allow for clarification of methods used to conduct titrations and eliminate confusion surrounding the terminology associated with alkalinity.

- If a pH value is reported, the conditions for which it is measured should be clearly identified (temperature, whether or not the sample is equilibrated with ambient conditions or with CO_2 sparge).
- The titration method used (ASTM 1067D titration or equivalence point titration with d(pH)/d(C)) should be reported and the endpoint should be listed on the water chemistry if an endpoint titration was used. This is probably the most important recommendation to avoid misinterpretation of the reported alkalinity value.

- The alkalinity should be reported in molar (standardized unit) to avoid the confusion between ppm$_w$ HCO_3^- or ppm$_w$ $CaCO_3$.
- A full measured list of organic acids reported in molar should be included with each water chemistry document.

Furthermore, if industry adopted a more standardized field brine chemistry data sheet, consistency between labs would become more apparent.

Chapter 7: Conclusions and Future Work

The methodologies commonly used to determine the alkalinity of brines containing bicarbonate and carboxylate salts were reviewed and reproduced. The hypotheses proposed in Chapter 3.2 could be tested and are reviewed in the following.

Hypothesis 1 is true - An endpoint titration at pH 4.5 should not be used to represent the true equivalence point for the titrations on brines of unknown composition. Alkalinity values taken at pH 4.5 may underestimate the true alkalinity and lead to erroneous corrosion predictions. Using the lower alkalinity value for corrosion prediction will result in a higher corrosion rate. Lower corrosion rates will correspond to a more cautious, maybe too conservative, prediction of corrosion rate, resulting in the use of more inhibitor than is necessary. Brine samples should be properly titrated from their original pH to a final pH of 2.0, to avoid missing equivalence points and increase the accuracy of alkalinity measurements in corrosion prediction models.

Hypothesis 2 is true - Titration curves of solutions involving a wide variety of carboxylate salts can be properly modelled over the entire pH range using the Rice or Henderson equation methods. The presence of carboxylate salts will tend to flatten the titration curve and make the visual interpretation of the results difficult, with no clear equivalence point. The use of a modeled titration curve, especially following the Rice methodology, can greatly facilitate the interpretation of the results.

Hypothesis 3 is not validated - The presence of high salt content was not observed to flatten the titration curve and make the visual interpretation of the results more difficult. The presence of high salt in titration curves could not be properly modeled at low values of pH. The use of an activity-based model was used to better represent the chemical species in solution allowing for better comparisons at higher values of pH. The understanding of how ionic strength contributes to a higher measured value of alkalinity is not well defined and should be studied in future work.

Currently, oil and gas field operators still produce water chemistry documents with alkalinity measurements taken to pH 4.5, from colorimetric and endpoint titrations based on the ASTM 1067D standard. The modification of the ASTM 1067D standard is not suggested, but avoid using the standard when conducting titrations of oilfield brines. The modification of the suggested endpoint (pH 4.5) to a lower pH would result in corrosion estimations with less safety margins. Based on the importance titrations are always needed for the highest accuracy of alkalinity and the corresponding corrosion rate.

Even if this is not ideal, it is possible to estimate the true value of alkalinity from modelled titration curves, using the alkalinity at pH 4.5 as an “anchor” point and other water chemistry information, such as the organic acid content and the salt concentration. Future research should focus developing such calculation routines using the Rice methodology.

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Chapter 9: Appendix

9.1 OLI Activity Coefficients Using the MSE model.

The Mixed solvent electrolyte model is incorporated into OLI systems software package for use with mixed electrolyte systems. The model predicts the activity coefficients of dilute to concentrated electrolyte salt systems with multiple components. Chemical equilibrium is used to account for chemical speciation in multiphase, and multicomponent systems using expressions for excess gibs free energy.

The following activity coefficients were used for a sample solution containing 0.01 M $NaHCO_3$, and 0.0085 M CH_3COONa at 0.5-2 M ionic strengths. Activity coefficients calculated using the MSE model are both pH and solution specific. Therefore, three separate regions of activities coefficients were considered to account for a wide range of pH values during titration. The regions of activities coefficient that were considered include initial – 4.5 pH, 4.49 – 3 pH, and 2.99 – low pH. Tables below list the applicable activity coefficients to be implemented with the Rice equation under non-ideal conditions when activities are not assumed equal to one.

Table 13: *Activity coefficients obtained at pH 7.7 from the MSE model in OLI used for analysis of brines from an initial – 4.5 pH, mol/L reference state.*

NaCl (Ionic strength)	**0.5 M**	**1.0 M**	**1.5 M**	**2.0 M**
γ_{H+}	0.759	0.799	0.865	0.975
γ_{HCO3-}	0.591	0.536	0.426	0.380
γ_{CO2}	1.09	1.19	1.28	1.40
γ_{Ac-}	0.668	0.632	0.615	0.620
γ_{HAc}	1.09	1.19	1.28	1.40
γ_{OH-}	0.729	0.740	0.770	0.833

Table 14: *Activity coefficients obtained at pH 5.3 from the MSE model in OLI used for analysis of brines from 4.49 – 3.0 pH, mol/L reference state.*

NaCl (Ionic strength)	**0.5 M**	**1.0 M**	**1.5 M**	**2.0 M**
γ_{H+}	0.831	0.957	1.106	1.302
γ_{HCO3-}	0.634	0.573	0.528	0.502
γ_{CO2}	0.149	0.099	0.075	0.063
γ_{Ac-}	0.806	0.897	1.000	1.133
γ_{HAc}	1.268	1.554	1.853	2.222
γ_{OH-}	0.598	0.525	0.478	0.455

Table 15: *Activity coefficients obtained at pH 2.5 from the MSE model in OLI used for analysis of brines from 2.99 – low pH, mol/L reference state.*

NaCl (Ionic strength)	**0.5 M**	**1.0 M**	**1.5 M**	**2.0 M**
γ_{H+}	0.832	0.958	1.11	1.30
γ_{HCO3-}	0.634	0.573	0.528	0.502
γ_{CO2}	1.10	1.20	1.29	1.40
γ_{Ac-}	0.806	0.897	1.00	1.13
γ_{HAc}	1.27	1.56	1.86	2.23
γ_{OH-}	0.598	0.525	0.478	0.455

9.2 Derivation of the Henderson Equation

The derivation of the Henderson equation is shown below, starting with the electroneutrality equation for species present in solution, Equation 4. The influence of CO_3^{2-} is considered to be small and is neglected. Considering an aqueous solution containing dissolved $NaHCO_3$ and CH_3COONa, the electroneutrality writes as:

$$0 = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [Ac^-] - [Na^+] - [H^+]$$

$$0 = [HCO_3^-] + \cancel{2[CO_3^{2-}] + [OH^-]} + [Ac^-] - [Na^+] - [H^+]$$

When the titration is performed, HCl is added and is expressed as the molar concentration of Cl^- [35].

$$[Cl^-] = [H^+] + [Na^+] - [HCO_3^-] - [Ac^-]$$

The molar concentration of Na^+ in solution represents the total $NaHCO_3$ and CH_3COONa concentration since Na^+ is added in the same molar ratio when preparing solutions.

$$[NaHCO_3] = [H_2CO_3]_T$$

$$[Na\mathrm{CH_3COO}] = [HAc]_T$$

The relation between total species concentration and the undissociated acid and conjugate base concentration is as follows:

$$[HA_{free}] = [A^-] + [H^+]$$

and,

$$[A^-] = \frac{[HA_T]}{10^{pka-pH} + 1}$$

$$[HA] = \frac{[HA_T]}{10^{pH-pka} + 1}$$

Using terms to represent the total carbonate and acetate species and substituting into the electroneutrality equation, the following equation can be written:

$$[Cl^-] = [H^+] + ([H_2CO_3]_T - [HCO_3^-]) + ([HAc]_T \ - [Ac^-])$$

$$[Cl^-] = [H^+] + [H_2CO_3]_{free} + [HAc]_{free}$$

The final equation becomes:

$$HCl(M, calc) = 10^{-pH} + \frac{[H_2CO_3]_T}{\frac{K_{ca}}{10^{-pH}} + 1} + \frac{[HAc]_T}{\frac{K_{HAc}}{10^{-pH}} + 1} = 10^{-pH} + \frac{T_{HCO3-}}{\frac{K_{ca}}{10^{-pH}} + 1} + \frac{T_{Ac-}}{\frac{K_{HAc}}{10^{-pH}} + 1}$$