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ALKALINITY IN OIL FIELD WATERS WHAT ALKALINITY IS AND HOW IT IS MEASURED

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ABSTRACT

The alkalinity is an important parameter in the description of pH-behaviour, buffer capacity and scaling potentials in oil field waters. Although the alkalinity is widely used, it seems to be considerable confusion in connection with the concept. It is often used incorrectly and different authors define the concept in different ways. Several different methods for the determination of alkalinity can be found in the literature.

In this paper, we discuss the definition of alkalinity and how to use alkalinity in oil field waters to obtain data of importance for scale and pH predictions. We also show how a simple titration of oil field waters can give both the alkalinity and the content of organic acids in these waters. It is obvious from our findings that most of the methods used today may give considerable errors when applied to oil field waters with high contents of organic acids.

INTRODUCTION

Alkalinity is an important parameter used to describe composition, buffer capacity and pH-behaviour of waters in many different fields of science, such as biology, geology and medicine. Although the alkalinity is widely applied, it seems to be a lot of confusion in connection with the concept, and it is often used incorrectly. One of the reasons for all the confusion is probably due to the first use of this concept to describe fresh water systems containing bicarbonate and carbonate only. In this case, when pH is between 3.5-9, the alkalinity will have the same numerical value as the bicarbonate concentration. Due to this fact the alkalinity concept and the bicarbonate concentration have incorrectly been substituted for one another. Some workers have made an effort to clarify the notations, and the term bicarbonate alkalinity have been introduced (1, 2, 3). The bicarbonate alkalinity of a system means the contribution to the alkalinity from bicarbonate and carbonate, and is equal to the total alkalinity if no other weak acids are present. However, the term bicarbonate alkalinity does not have any physical meaning in a strict sence. It can be compared to a situation where we splitt pH into a carbonate-pH and an acetic acid-pH and total pH.

Several experimental methods are available for the determination of the alkalinity for a system where titration is the most common used (2, 3, 4). Pauss et al. (1) have reviewed 12 different methods based on titration or volumetric measurements of evolved CO₂. With only bicarbonate present, the titration end point is close to pH≈4.0-4.5 and in most of the published methods for alkalinity determination, the endpoint is given to be round this pH. But for systems containing other weak acids, like acetic acid (HAc), this titration method fails. The reason is simply that the presence of theses acids changes the end point pH. Another problem is that many procedures given for alkalinity determination are typical "how-to-measure-alkalinity-without-knowing-what-it-is"-methods. It is important to note that alkalinity has to be carefully defined for every new system studied.

To clarify the alkalinity concept, we want to present a proper definition. We want to discuss how the alkalinity of a solution is varying with additions of acids and bases, and finally we want to present a simple method to measure this property. The work will focus on alkalinity in typical oil field waters, since some misunderstandings of the concept have been observed by us during our contact with the oil industry.

THEORY

In aqueous systems roughly 4 groups of molecules and ions are related to the alkalinity

1. Neutral species: H_2O , $\text{CO}_2(\text{aq})$, $\text{CH}_3\text{COOH}(\text{aq})$, etc.
2. Dissociation products of water and weak acids: H^+ and OH^- , HCO_3^- , CH_3COO^- , HPO_4^{2-} , etc.
3. Dissociation products of strong acids: Cl^- , SO_4^{2-} etc.
4. Metallic cations: Na^+ , K^+ , Ca^{2+} , Mg^{2+} , etc.

For charged species, the equation of electro neutrality has to be fulfilled. This equation requires that the number of positive charges must equal the number of negative charges

$$\sum n_i \cdot [i] = 0 \quad (1)$$

where $[i]$ is the concentration and n_i is the charge of an ion i . As an example we may consider a water solution of NaCl , CaSO_4 , acetic acid (HAc) and dissolved CO_2 . Equation 1 then becomes

$$[\text{Na}^+] + 2 \cdot [\text{Ca}^{2+}] + [\text{H}^+] = [\text{OH}^-] + [\text{Cl}^-] + 2 \cdot [\text{SO}_4^{2-}] + [\text{HCO}_3^-] + 2 \cdot [\text{CO}_3^{2-}] + [\text{Ac}^-] \quad (2)$$

If eq 2 is rearranged such that all pH dependent species (group 2) are on the right side, and all other species (group 3 and 4) are on the left, this gives a definition of the total alkalinity

$$A_T = [\text{Na}^+] + 2 \cdot [\text{Ca}^{2+}] - [\text{Cl}^-] - 2 \cdot [\text{SO}_4^{2-}] = [\text{HCO}_3^-] + 2 \cdot [\text{CO}_3^{2-}] + [\text{Ac}^-] + [\text{OH}^-] - [\text{H}^+] \quad (3)$$

Where subscript T indicates total alkalinity. pH dependent means that the ion can participate in protonation or dissociation reactions which will influence the pH of the solution. The ions on the left side of eq 3, Na^+ , Cl^- etc., are not dependent on pH, and their concentrations are constant if pH changes. At this point, it is important to note that pH in oil field waters vary between $\approx 3-8$. Species with a pK_a value outside this range are completely dissociated or undissociated. That is why $[\text{SO}_4^{2-}]$ is regarded to be a constant in eqs 2-3. At the extreme ends of the pH scale, however, almost every ion can participate in some kind of acid-base reactions. This is also the reason why it is not practical, or possible, to make an absolute definition of alkalinity. It has to be defined for every system taking into consideration which components are present and under which condition the concept is applied. The alkalinity equation is normally written as

$$A_T = [\text{HCO}_3^-] + 2 \cdot [\text{CO}_3^{2-}] + [\text{Ac}^-] + [\text{OH}^-] - [\text{H}^+] \quad (4)$$

Another way of viewing alkalinity is to say that the alkalinity equals the sum of titratable bases. $[\text{H}^+]$ is then treated as a proton source and enters therefore eq 4 with a negative sign. Remember that H^+ is a short hand notation for protonated water, H_3O^+ . If the solution contains ammonia, NH_4^+ should be treated as a proton source and enter eq 4 with a negative sign, rather than treating NH_3 as a titratable base. The reason for this is that we want to use the equation of neutrality when defining the alkalinity. As we will see later this leads to the comfortable situation that evaporation from the solution of acidic or basic gases will not change the alkalinity.

How is alkalinity changed?

At first sight, it is easy to believe that an addition of an acid HAc will raise the alkalinity, since $[Ac^-]$ enters the equation. This is, however, not true. When HAc dissociates, an equal number of moles of H^+ and Ac^- are produced, and the change in alkalinity is zero. The result is identical for CO_2 . If CO_2 dissolves and dissociates, it produces identical number of moles of HCO_3^- and H^+ or CO_3^{2-} and twice as many H^+ . Since CO_3^{2-} is double charged and multiplied by 2, the change in alkalinity is again zero. It is also obvious that an addition of NaCl or $CaSO_4$ does not change the alkalinity since non of these ions enters eq 4. The only way to change the alkalinity is therefore to add a compound which when dissociates produces ions that enters eq 3 on both sides of the equality sign. Examples are $NaHCO_3$, NaAc, $CaCO_3$, NaOH, HCl etc. All these compounds will increase the alkalinity except the addition of HCl which will result in a reduced alkalinity. If enough HCl is added the alkalinity will in fact become zero and then negative. Equation 4 also shows that pure water has zero alkalinity since in pure water $[H^+] = [OH^-]$ and no other species are present in eq 4.

Alkalinity and carbonate precipitation

$CaCO_3$ may precipitate from waters rich in calcium and bicarbonate. Such precipitates may be troublesome for technical reasons i household equipment, industrial hot water systems and during oil recovery from oil fields rich in carbonaceous rocks. Oil is very often produced together with water, and when the CO_2 pressure and temperature of this water is reduced, $CaCO_3$ will form. To be able to estimate the carbonate scaling potential of a given water, the saturation index of such a water is estimated. The saturation index is defined through eq 5.

$$SI(CaCO_3) = \ln \left[\frac{[Ca^{2+}] \cdot [CO_3^{2-}]}{K_{Sp}(CaCO_3)} \right] \quad (5)$$

In this equation $K_{Sp}(CaCO_3)$ is the stoichiometric solubility product of $CaCO_3$ at a given temperature, pressure and ionic strength. When alkalinity increases the carbonate scaling potential may increase by several orders of magnitude. Typical oil field waters have alkalinities in the range 10-20 mmol/l (5). Figure 1 shows how important good alkalinity determinations are for accurate carbonate scaling predictions.

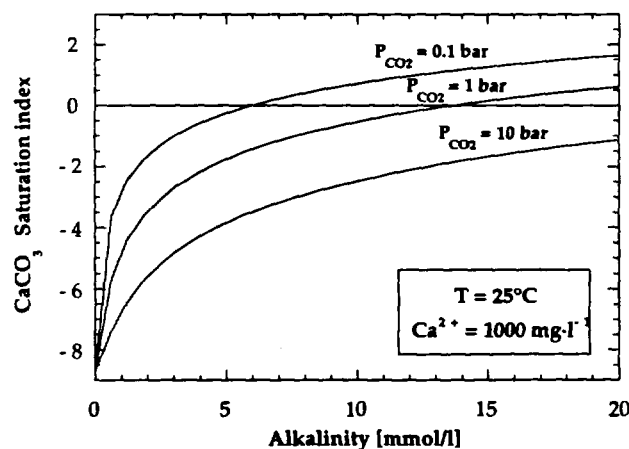


Figure 1. Saturation index $\ln \left[\frac{[Ca^{2+}] \cdot [CO_3^{2-}]}{K_{Sp}(CaCO_3)} \right]$ for $CaCO_3$ as a function of alkalinity for 3 different CO_2 pressures at $25^\circ C$ and $[Ca^{2+}] = 1000 \text{ mg}\cdot\text{l}^{-1}$. Calculations are done with a scale prediction computer program (8).

Alkalinity determinations

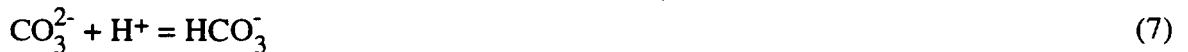
It may seem possible to calculate the alkalinity from the concentrations of the species on the left side of eq 3. Theoretically this is possible, but the alkalinity will then appear as a small difference between large numbers since Na^+ and Cl^- concentrations are typically ≈ 50 times greater than A_T . An error of 1% in the Na^+ concentration will result in a 50% error in A_T . It is therefore better to determine the sum of the concentrations in eq 4 by titration. Many different titration methods have been published. Most of these methods are based on the titrations given below

- Titration with HCl to some end point, normally given to be pH = 4.5 or 4.3 (1, 3)
- Adding HCl to pH \approx 2-4, boiling or flushing with nitrogen to evaporate CO_2 , and then back titration with NaOH (5).

Our aim is to show that a combination of the two methods will give very good measurements of both the alkalinity and the content of organic acids in the water when these acids have roughly the same dissociation constants. The reaction mechanism of the overall titration reaction is



This reaction can be divided in four elementary steps



The two first reactions are fast and complete for pH < 4.5-4.3 since $\text{pK}_a(1) = 10.33$ and $\text{pK}_a(2) = 6.35$ at 25°C (7). The two last reactions are, however, slow and there can be a substantial supersaturation of CO_2 in the water, even at low pH. To remove CO_2 , the solution must therefore be boiled for a few minutes (6) or flushed with nitrogen (5).

The alkalinity of a solution is decreasing with HCl and increasing with NaOH additions, respectively. The alkalinity during a titration with HCl, A_T^{HCl} , is related to the alkalinity in the original sample, A_T° , through

$$A_T^{\text{HCl}} = \frac{A_T^\circ V^\circ - V_{\text{HCl}}[\text{HCl}]}{V^\circ + V_{\text{HCl}}} \quad (11)$$

where V° = volume of sample, V_{HCl} = volume of HCl added. During the back titration with NaOH

$$\begin{aligned} A_T^{\text{NaOH}} &= \frac{A_T^{\text{HCl}}(V^\circ + V_{\text{HCl}}) + V_{\text{NaOH}}[\text{NaOH}]}{V^\circ + V_{\text{HCl}} + V_{\text{NaOH}}} \\ &= \frac{A_T^\circ V^\circ - V_{\text{HCl}}[\text{HCl}] + V_{\text{NaOH}}[\text{NaOH}]}{V_{\text{tot}}} \end{aligned} \quad (12)$$

where V_{NaOH} = volume of NaOH added and $V_{\text{tot}} = V^\circ + V_{\text{HCl}} + V_{\text{NaOH}}$. Since the alkalinity is always given by eq 4, a combination of eq 4 and 12 and rearranging gives

$$A_T^\circ = \left([\text{HCO}_3^-] + 2 \cdot [\text{CO}_3^{2-}] + [\text{Ac}^-] + [\text{OH}^-] - [\text{H}^+] \right) \frac{V_{\text{tot}}}{V^\circ} + \frac{V_{\text{HCl}}[\text{HCl}] - V_{\text{NaOH}}[\text{NaOH}]}{V^\circ} \quad (13)$$

This equation can theoretically be used to calculate the alkalinity at any stage of the titration process. This is unfortunately very difficult in practice because

- The total amount of carbonic and organic acids are unknown.
- Deviation from ideality in the water mixture of any components or ions on the right hand side of eq 13.

The first problem can be reduced by a titration to $\text{pH} < 3.5$ where the concentrations of HCO_3^- , CO_3^{2-} , OH^- and Ac^- are very small. H^+ can be calculated from pH measurements. The second problem is, however, more difficult to handle. A pH measurement gives the H^+ activity in the solution, not the concentration. In eq 13, however, concentrations are given. If these concentrations are too high or the solution has a high ionic strength, corrections for deviation from ideality have to be made. Even if this deviation is only 5%, an error in the calculated alkalinity may be as large as 5%. It is very difficult to make accurate activity coefficient corrections. It is easier to perform the titration in such a way that a small error in the calculated alkalinity is obtained. To achieve this minimum error we have to end the titration where the buffer capacity of the solution is low. The buffer capacity, β , is given by

$$\beta = \frac{d(C_{\text{NaOH}}^\circ - C_{\text{HCl}}^\circ)}{dpH} = 2.30 \cdot \left[[\text{H}^+] + [\text{OH}^-] + \sum_i \frac{[\text{Acid}_i] \cdot [\text{Base}_i]}{C_i^\circ} \right] \quad (14)$$

Titration end points

A water sample from a typical oil field water contains both bicarbonate and organic acids together with ions typical for sea- and formation-waters. The pH of the sample is typically 7-8 and the ionic strength $\approx 0.5\text{M}$. To find the titration end points, it is practical to use a log-log diagram. Figure 2 shows such a diagram for a system containing 16.5 mmol/l H_2CO_3 and 8.33 mmol/l HAc. Figure 3 and 4 shows similar diagrams where the concentration of organic acid and carbonic acid is zero, respectively. The buffer capacity is plotted as $\log \frac{\beta}{2.30}$.

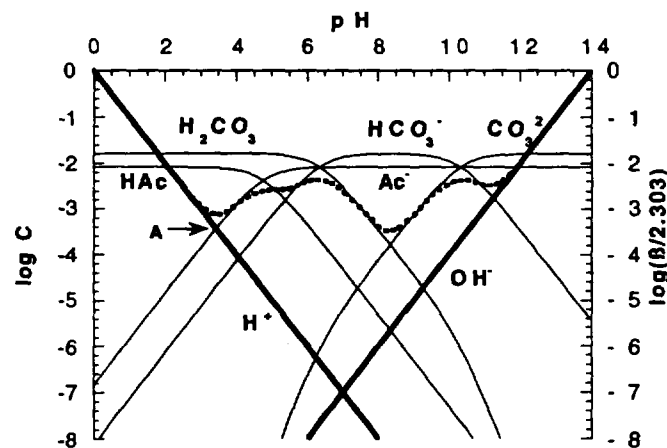


Figure 2. Log-log diagram for a system containing 16.5 mmol/l NaHCO_3 and 8.33 mmol/l (500 mg/l) HAc. The full drawn lines give the concentrations of H^+ , OH^- , HAc, Ac^- , H_2CO_3 , HCO_3^- and CO_3^{2-} . The dotted line gives the buffer capacity β as $\log(\beta/2.30)$.

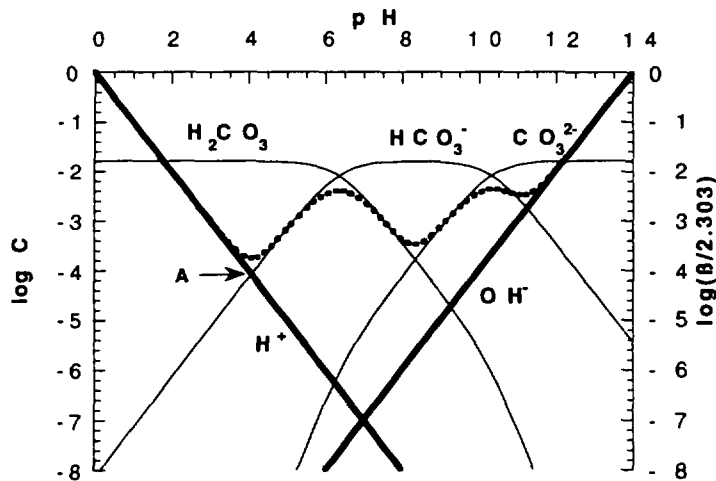


Figure 3. Log-log diagram for a system containing 16.5 mmol/l NaHCO₃.
 -: log(concentrations), ---: log(B/2.303)

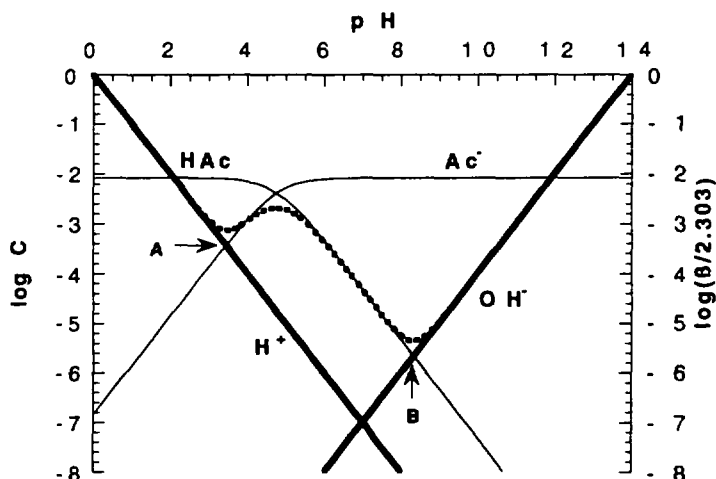


Figure 4. Log-log diagram for a system containing 8.33 mmol/l (500 mg/l) HAc.
 -: log(concentrations), ---: log(B/2.303)

During the HCl titration, the pH will decrease, and an end point is found at pH≈3.5-4, depending on the system composition. There are three possibilities, all marked with an A in Figures 2-4. The conditions for these end points are given in Table 1.

Table 1. Conditions for end points during titration with HCl.

System	Condition for end point	Reference
H ₂ CO ₃ and HAc	$[\text{HCO}_3^-] + [\text{Ac}^-] = [\text{H}^+]$	Figure 2
H ₂ CO ₃	$[\text{HCO}_3^-] = [\text{H}^+]$	Figure 3
HAc	$[\text{Ac}^-] = [\text{H}^+]$	Figure 4

In all three cases all other concentrations in the paranthesis of eq 13 are small, and the paranthes is close to zero. Since $V_{\text{NaOH}} = 0$, eq 13 reduces to

$$A_T^\circ = \frac{V_{\text{HCl}}^{\text{A}}[\text{HCl}]}{V^\circ} \quad (15)$$

$V_{\text{HCl}}^{\text{A}}$ is the volume of HCl added to reach point A shown in Figures 2-4. The pH at A can in all three cases be calculated using eq 16.

$$\text{pH}_A = -1/2 \log \left[K_{\text{HAc}} \cdot [\text{HAc}]_{\text{tot}} + K_{\text{H}_2\text{CO}_3} \cdot [\text{H}_2\text{CO}_3]_{\text{tot}} \right] \quad (16)$$

where $K_{\text{HAc}} = [\text{H}^+] \cdot [\text{Ac}^-] / [\text{HAc}]$ and $K_{\text{H}_2\text{CO}_3} = [\text{H}^+] \cdot [\text{HCO}_3^-] / [\text{H}_2\text{CO}_3]$. The subscript tot means total concentration of the different species. This concentration is somewhat smaller than the original concentration due to dilution during titration. We can relate these concentrations through the equation

$$[i]_{\text{tot}} = [i]_{\text{tot}}^\circ \cdot \frac{V^\circ}{V_{\text{tot}}} \quad (17)$$

where $[i]_{\text{tot}}$ is the total concentration of eg. CO_2 dissolved ($[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$). The superscript $^\circ$ indicate initial concentration and V° and V_{tot} are the solution volumes before and after titration, respectively. The total concentration of dissolved CO_2 in the sample, $[\text{H}_2\text{CO}_3]_{\text{tot}}^\circ$, can be calculated using the initial mass balance for H_2CO_3

$$\begin{aligned} [\text{H}_2\text{CO}_3]_{\text{tot}}^\circ &= [\text{H}_2\text{CO}_3]^\circ + [\text{HCO}_3^-]^\circ + [\text{CO}_3^{2-}]^\circ \\ &= [\text{HCO}_3^-]^\circ \cdot \left(\frac{[\text{H}^+]^\circ}{K_{\text{H}_2\text{CO}_3}} + 1 + \frac{K_{\text{HCO}_3^-}}{[\text{H}^+]^\circ} \right) \end{aligned} \quad (18)$$

where $K_{\text{HCO}_3^-} = [\text{H}^+] \cdot [\text{CO}_3^{2-}] / [\text{HCO}_3^-]$. Since pH in samples from normal oil field waters is $\approx 7-8$, $[\text{H}_2\text{CO}_3]^\circ$, $[\text{CO}_3^{2-}]^\circ$, $[\text{OH}^-]^\circ$, $[\text{H}^+]^\circ$ and $[\text{HAc}]^\circ$ are small and $[\text{HCO}_3^-]^\circ$ can be estimated by rearranging eq 4

$$[\text{HCO}_3^-]^\circ \approx A_T^\circ - [\text{Ac}^-]^\circ \approx A_T^\circ - [\text{HAc}]_{\text{tot}}^\circ \quad (19)$$

where the total amount of organic acid in the sample, $[\text{HAc}]_{\text{tot}}^\circ$, is given by the initial mass balance $[\text{HAc}]_{\text{tot}}^\circ = [\text{HAc}]^\circ + [\text{Ac}^-]^\circ$. Since CO_2 is easily removed by boiling the solution at low pH, we added HCl to reach $\text{pH} \approx 2.2$. The total volume of added HCl is called V_{HCl} . If no weak organic acids are present in the solution, the back titration is a simple titration of HCl with NaOH which ends at $[\text{OH}^-] = [\text{H}^+]$, eg. $\text{pH} = 7$. Since all H_2CO_3 now is removed and $[\text{OH}^-] = [\text{H}^+]$, the paranthes in eq 13 is zero and eq 13 reduces to

$$A_T^\circ = \frac{V_{\text{HCl}}[\text{HCl}] - V_{\text{NaOH}}[\text{NaOH}]}{V^\circ} \quad (20)$$

where V_{NaOH} is the volume of NaOH added to reach pH=7. If HAc is present there are two end points during the backtitration with NaOH. The first, A, is reached when $[\text{Ac}^-] = [\text{H}^+]$ (see Figure 4). In this case eq 13 reduces to eq 21 and the pH at the end point is calculated from eq 16, setting $[\text{H}_2\text{CO}_3]_{\text{tot}}$ equal to zero.

$$A_T^\circ = \frac{V_{\text{HCl}}[\text{HCl}] - V_{\text{NaOH}}^{\text{A}}[\text{NaOH}]}{V^\circ} \quad (21)$$

The second end point, B (see Figure 4), is reached when $[\text{HAc}] = [\text{OH}^-]$ and can be calculated from eq 22.

$$\text{pH}_B = 1/2 \cdot \log \left[\frac{[\text{HAc}]_{\text{tot}}}{K_w \cdot K_{\text{HAc}}} \right] \quad (22)$$

At titration point B, $[\text{Ac}^-]$ is much larger than all other concentrations and eq 13 reduces to

$$A_T^\circ = [\text{Ac}^-] \frac{V_{\text{tot}}}{V^\circ} + \frac{V_{\text{HCl}}[\text{HCl}] - V_{\text{NaOH}}^{\text{B}}[\text{NaOH}]}{V^\circ} \quad (23)$$

Where $[\text{Ac}^-]$ is very close to the total concentration of acetic acid in the solution, $[\text{HAc}]_{\text{tot}}$ and $V_{\text{NaOH}}^{\text{B}}$ is the volume of NaOH added to reach the titration point B in Figure 4. To be able to calculate the alkalinity from this end point, it is therefore necessary to know the total amount of HAc present. Combination of eq 17 and 23 gives

$$A_T^\circ = [\text{HAc}]_{\text{tot}}^\circ + \frac{V_{\text{HCl}}[\text{HCl}] - V_{\text{NaOH}}^{\text{B}}[\text{NaOH}]}{V^\circ} \quad (24)$$

which is identical to the expression given by Oddo and Tomsen (5).

We have presented a procedure where three titrations give information about the solution alkalinity; eq 15, 20/21 and 24. The concentration of organic acid can also be calculated from these equations. $[\text{HAc}]_{\text{tot}}^\circ$ may be obtained using the alkalinity already calculated from eq 15 and 21 as outlined below.

To find the above titration end points for accurate determination of the alkalinity and the acid content is not straight forward since these end points depend on the total amounts of both carbonic acid and organic acid in the solution as described above. We need, however, only to have a rough estimate of the alkalinity and the organic acid concentration to estimate reasonable end points. A 50% error in the estimated concentrations will only result in an error of ≈ 0.15 pH units for the end point pH. The titration should therefore be performed with several pH readings around the expected end points. The obtained results can then be used to calculate the alkalinity and the organic acid concentration, and better end points may be estimated. By repeating the calculation procedure 2-4 times, the result will rapidly converge. The procedure can be summarised in 4 steps:

- Alkalinity and organic acid concentration are estimated. If the organic acid concentration is measured by other methods, this concentration is used.
- Titration end points are calculated:
 - pH_A from eq 16
 - pH_A from eq 16 with [H₂CO₃]_{tot}=0
 - pH_B from eq 22
- The titration results at pH_A are used to calculate the alkalinity from eq 15 and 20/21. If [HAc]_{tot}^o is unknown, this alkalinity is used to calculate [HAc]_{tot}^o from eq 24. If [HAc]_{tot}^o is known, the alkalinity can also be calculated from eq 24 with titration result at pH_B. The approximation [HCO₃⁻]^o ≈ A_T^o - [HAc]_{tot}^o and eq 17-18 is then used to obtain [H₂CO₃]_{tot}.
- A repetition from step 2 is applied until the data converge.

To test the above procedure some simple experiments were performed.

EXPERIMENTAL

pH measurements were performed with a Radiometer pHG201 glass electrode, and a REF201 reference electrode connected to a pHM92 pH meter. The burette used was a ordinary 50 ml burette with accuracy ±0.03ml. All chemicals were of p.a. quality with purity >99.5%. 0.1M HCl and NaOH were made from commercial standard solutions with ±0.5% accuracy.

The test solutions contained NaCl, NaAc, HAc and NaHCO₃ to give the solutions given in Table 2.

Table 2. Composition of test solutions.

Solution nr	NaCl [mmol/l]	NaHCO ₃ [mmol/l]	HAc [mmol/l]	NaAc [mmol/l]	A _T ^o [mmol/l]	[HAc] _{tot} ^o [mmol/l]
1	500	16.52	0	0	16.52	0
2	500	16.36	8.58	0	16.36	8.58
3	500	8.05	0	8.49	16.54	8.49

The titrations were performed by titrating 100 ml of the test solutions with 0.1M HCl to pH≈2.2. The solution were then boiled in 5 minutes with reflux and then back titrated with 0.1M NaOH. After each addition of HCl or NaOH, the solution was allowed to equilibrate. When the pH meter indicated a stable value, this pH was recorded. To test if the effect of boiling was significant, two titrations were performed. After addition of HCl to pH≈2.2, only one of the solutions were boiled. Then the solutions were back titrated with NaOH. We found that boiling and the use of reflux when boiling was necessary to obtain good data. With no reflux the HAc content determined was 3-3.5% too low due to loss of acid through evaporation.

RESULTS

The essential experimental data are summarized in Figures 5-8. The importance of boiling the solution to remove CO₂ is clearly seen in Figure 5. During back titration, the difference is observed. With no boiling the titration curve has a plateau at pH≈6, which corresponds to the first dissociation constant for H₂CO₃, indicating dissolved CO_{2(aq)} in the sample. The boiled solution, however, shows a sharp increase in pH round pH≈8, corresponding to the end point of the titration of HAc.

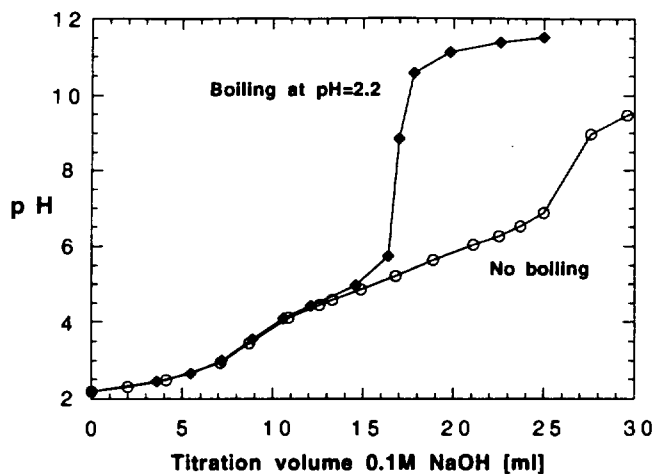


Figure 5. Titration curves from titration of solution nr 2 showing the effect of boiling the sample at pH=2.2 before back titration with NaOH.

Titration results

The three solutions given in Table 2 were titrated with both HCl and NaOH as explained above. Results are shown in Figures 6-8. The calculations were performed according to the iterative procedure given above. As an initial guess for A_T° and $[HAc]_{tot}^{\circ}$, we arbitrarily used 10 and 2 mmol/l respectively. These initial values were used in eq 19 \rightarrow 18 \rightarrow 17 \rightarrow 16 to calculate pH at the end points. These are given in the first row in Table 3; $pH_A = 3.71$, $pH_A = 3.73$ and $pH_B = 8.03$. By interpolation in the titration curve for solution 1 in Figure 6, the titration volumes V_{HCl}^A , V_{NaOH}^A and V_{NaOH}^B were calculated to be 16.76 ml, 9.03 ml and 9.46 ml, respectively. Equation 15 and 21 were used to calculate alkalities and the average value was 16.87 mmol/l. This value and V_{NaOH}^B were used in eq 24 to calculate $[HAc]_{tot}^{\circ} = 0.33$ mmol/l.

In the next iteration step these new values for A_T° and $[HAc]_{tot}^{\circ}$ were used to calculate better end points given as $pH_A = 3.97$, $pH_A = 4.19$ and $pH_B = 7.57$, in the second row in Table 3. The procedure was then repeated until the data converge. As can be observed from the data in Table 3, is the calculated amount of organic acid after the third iteration step so small that we assumed it to be zero. The endpoint for the back titration is then pH=7.00 and eq 15 and 20 are used to calculate the alkalinity. The same procedure was used for solution 2 and 3. The calculations are shown in detail in Table 4 and 5.

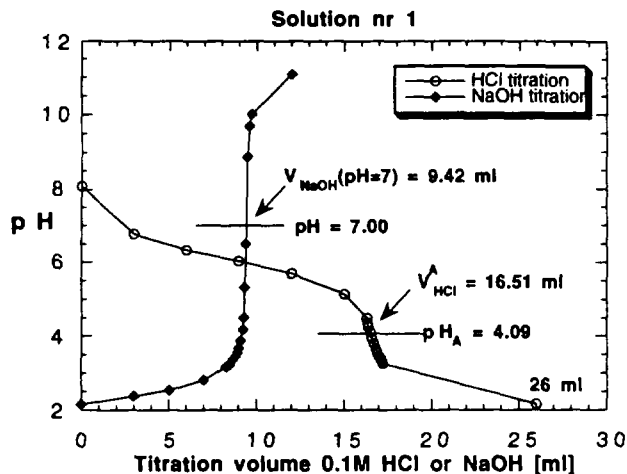


Figure 6. Titration curves from titration of solution nr 1 with 0.1M HCl and NaOH. The horizontal lines show the end point pH's and the titration volumes are found by interpolation in the titration curve.

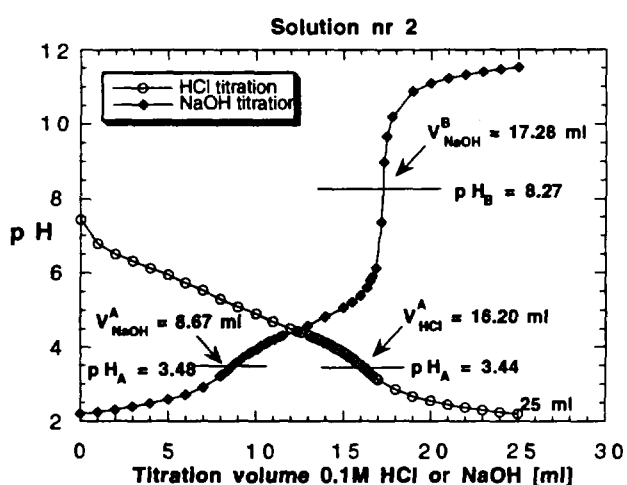


Figure 7. Titration curves from titration of solution nr 2 with 0.1M HCl and NaOH. The horizontal lines show the end point pH's and the titration volumes are found by interpolation in the titration curve.

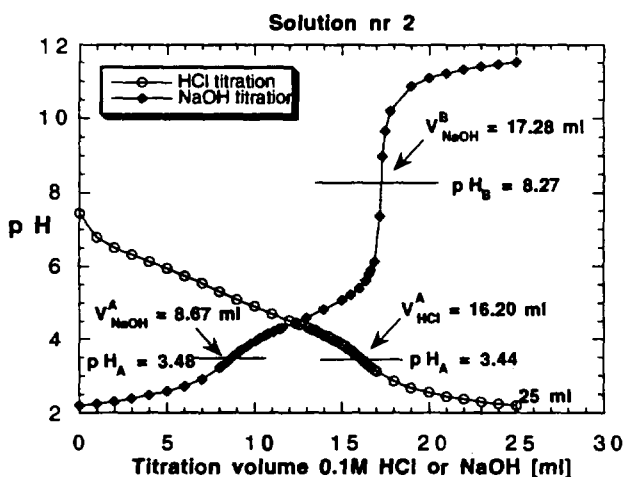


Figure 8. Titration curves from titration of solution nr 3 with 0.1M HCl and NaOH. The horizontal lines show the end point pH's and the titration volumes are found by interpolation in the titration curve.

Table 3. Calculated titration data for solution nr 1 using first 0.1 M HCl and then 0.1 M NaOH.

Sample:		Solution nr. 1		Initial guesses:	
Total HCl added:		26.00 ml		$[\text{HAc}]_{\text{tot}} = 2 \text{ mmol/l}$	
Initial pH:		8.08		$A_T = 10 \text{ mmol/l}$	
Calc. end point pH		Calculated volumes [ml]		A_T [mmol/l]	Results [mmol/l]
1	pH _A 3.71	V _{HCl} ^A 16.76	16.76	16.76	A _T (avrg) 16.87
	pH _A 3.73	V _{NaOH} ^A 9.03	16.97	16.97	[HAc] _{tot} 0.33
	pH _B 8.03	V _{NaOH} ^B 9.46			[H ₂ CO ₃] _{tot} 16.94
2	pH _A 3.97	V _{HCl} ^A 16.58	16.58	16.58	A _T (avrg) 16.67
	pH _A 4.19	V _{NaOH} ^A 9.25	16.75	16.75	[HAc] _{tot} 0.10
	pH _B 7.57	V _{NaOH} ^B 9.44			[H ₂ CO ₃] _{tot} 16.96
3	pH _A 4.05	V _{HCl} ^A 16.53	16.53	16.53	A _T (avrg) 16.62
	pH _A 4.43	V _{NaOH} ^A 9.29	16.73	16.73	[HAc] _{tot} 0.05*
	pH _B 7.32	V _{NaOH} ^B 9.43			[H ₂ CO ₃] _{tot} 16.97
4	pH _A 4.09*	V _{HCl} ^I 16.51	16.51	16.51	A _T (avrg) 16.55
	pH=7 7.00*	V _{NaOH} 9.42	16.58	16.58	[HAc] _{tot} 0.00 Error A _T +0.2% Error [HAc] ^o -

* Assume no HAc present

Table 4. Calculated titration data for solution nr 2 using first 0.1 M HCl and then 0.1 M NaOH.

Sample:		Solution nr. 2		Initial guesses:	
Total HCl added:		25.00 ml		$[\text{HAc}]_{\text{tot}} = 2 \text{ mmol/l}$	
Initial pH:		7.43		$A_T = 10 \text{ mmol/l}$	
Calc. end point pH		Calculated volumes [ml]		A_T [mmol/l]	Results [mmol/l]
1	pH _A 3.71	V _{HCl} ^A 15.47	15.47	15.47	A _T (avrg) 15.57
	pH _A 3.73	V _{NaOH} ^A 9.33	15.67	15.67	[HAc] _{tot} 7.83
	pH _B 8.03	V _{NaOH} ^B 17.26			[H ₂ CO ₃] _{tot} 8.39
2	pH _A 3.46	V _{HCl} ^A 16.16	16.16	16.16	A _T (avrg) 16.23
	pH _A 3.50	V _{NaOH} ^A 8.71	16.29	16.29	[HAc] _{tot} 8.51
	pH _B 8.25	V _{NaOH} ^B 17.28			[H ₂ CO ₃] _{tot} 8.37
3	pH _A 3.44	V _{HCl} ^A 16.20	16.20	16.20	A _T (avrg) 16.27
	pH _A 3.48	V _{NaOH} ^A 8.67	16.33	16.33	[HAc] _{tot} 8.55
	pH _B 8.27	V _{NaOH} ^B 17.28			[H ₂ CO ₃] _{tot} 8.37
4	pH _A 3.44	V _{HCl} ^A 16.20	16.20	16.20	A _T (avrg) 16.27
	pH _A 3.48	V _{NaOH} ^A 8.67	16.33	16.33	[HAc] _{tot} 8.55
	pH _B 8.27	V _{NaOH} ^B 17.28			Error A _T -0.6% Error [HAc] ^o -0.3%

Table 5. Calculated titration data for solution nr 3 using first 0.1 M HCl and then 0.1 M NaOH.

Sample:		Solution nr. 3		Initial guesses:		
Total HCl added:		25.00 ml		$[\text{HAc}]_{\text{tot}}^{\circ} = 2 \text{ mmol/l}$		
Initial pH:		8.30		$A_T^{\circ} = 10 \text{ mmol/l}$		
Calc. end point pH		Calculated volumes [ml]		A_T° [mmol/l]	Results [mmol/l]	
1	pH _A	3.71	V_{HCl}^A	15.72	A_T° (avrg)	15.81
	pH _A	3.73	V_{NaOH}^A	9.1	$[\text{HAc}]_{\text{tot}}^{\circ}$	7.93
	pH _B	8.03	V_{NaOH}^B	17.12	$[\text{H}_2\text{CO}_3]_{\text{tot}}^{\circ}$	8.55
2	pH _A	3.46	V_{HCl}^A	16.35	A_T° (avrg)	16.46
	pH _A	3.49	V_{NaOH}^A	8.43	$[\text{HAc}]_{\text{tot}}^{\circ}$	8.60
	pH _B	8.25	V_{NaOH}^B	17.14	$[\text{H}_2\text{CO}_3]_{\text{tot}}^{\circ}$	8.52
3	pH _A	3.44	V_{HCl}^A	16.42	A_T° (avrg)	16.51
	pH _A	3.48	V_{NaOH}^A	8.4	$[\text{HAc}]_{\text{tot}}^{\circ}$	8.65
	pH _B	8.27	V_{NaOH}^B	17.14	$[\text{H}_2\text{CO}_3]_{\text{tot}}^{\circ}$	8.52
4	pH _A	3.44	V_{HCl}^A	16.42	A_T° (avrg)	16.52
	pH _A	3.47	V_{NaOH}^A	8.38	$[\text{HAc}]_{\text{tot}}^{\circ}$	8.66
	pH _B	8.27	V_{NaOH}^B	17.14	Error A_T°	-0.1%
					Error $[\text{HAc}]^{\circ}$	2.0%

DISCUSSION

The end point pH is calculated using thermodynamic equilibrium constants, while we should have used the stoichiometric constants to correct for deviation from ideality. If we assume that there can be a $\pm 10\%$ deviation from ideality, that is $K_{\text{therm}} = K_{\text{stoich}} \pm 10\%$, and a 5% uncertainty in the total concentrations, this will, using Gauss law, result in a uncertainty in the calculated end point pH of ± 0.05 units. In addition there is a ± 0.05 units uncertainty in the pH determinations due to the difference in ionic strength between buffers used for calibration and the test samples. Since the titration curves are not very steep at the lower end point, an uncertainty in the titration volume of ± 0.15 ml will be the result. This results in an error in the alkalinity of ± 0.15 mmol/l which in the present case gives a relative error of $\pm 1\%$. This variation is also observed in the measured alkalinity. There is also some uncertainty in the reading of the titration volume (± 0.03 ml), in the HCl and NaOH concentrations ($\pm 0.5\%$) and in the sample volume (± 0.05 ml). By using Gauss law these uncertainties will give a relative error in the calculated HAc concentration of $\pm 1.8\%$. In the two titrations the relative error in HAc concentration was -0.3% and 2.0% , respectively. Equation 18 may be used to calculate the total amount of dissolved CO_2 in the solution, based on the initial pH. Due to possible deviations from ideality, this method is not very accurate. If, however, HAc is present in the solution it is the intersection between the $[\text{Ac}^-]$ and $[\text{H}^+]$ lines which determines the first end point and an error in $[\text{H}_2\text{CO}_3]_{\text{tot}}^{\circ}$ will not effect the calculated end point pH. If HAc is not present, the titration curve will be much steeper and an error in $[\text{H}_2\text{CO}_3]_{\text{tot}}^{\circ}$ is not that critical. This is easily seen when comparing the titration curves in Figure 6 and 7.

Solution nr 2 and 3 have almost the same alkalinity and the same total concentration of HAc. The organic acid was supplied as either HAc or NaAc, respectively. The results show no difference in the alkalinity determination. The HAc concentration, however, was only accurately determined in solution nr 2. This difference is probably a fortuitous effect. Theoretically, the only difference between these systems should be the initial pH.

It is important to boil the solution to remove all dissolved CO₂ before back titration. It is also important to use reflux due to the possible loss of HAc. It was easy to smell acetic acid in the vapour above a boiling solution. If the alkalinity is calculated using eq 22, as proposed by Oddo and Tomson (5), it is important to determine acid concentrations correctly since this concentration will influence the end point of the titration and therefore the measured alkalinity.

If the above method is used for oil field waters it is important to note that such waters may contain other organic acids like formic or propanoic acid, which will influence the titration end points. In this case, it is necessary to have an accurate determination of the content of all acids. The titration end point can then be calculated using an extended version of eq 16 where all acids are taken into consideration. However, the concentrations of other acids are normally much lower than acetic acid and they can therefore usually be neglected or treated as acetic acid since the variation in pK_a for these acids is small (7).

CONCLUSION

In the present work, we have proposed improvements in existing methods for alkalinity determinations of oil field waters. By a careful definition of the alkalinity, using a proper procedure to determine the correct titration end points and performing an accurate titration in small pH steps around the titration end point, it is possible to determine the alkalinity and organic acid concentration with a relative error of 1% and 2%, respectively. This improvement, selective to other published methods, is mainly based on the determination of the titration end points and the combination of both HCl and NaOH titrations. For most published methods, the titration is performed to some predefined end point, usually 4.3 or 4.5. This can cause considerable errors since the end point is dependent on the composition of the sample.

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