Experiment

ACID - BASE TITRATION CURVES

The CCLI Initiative

Computers in Chemistry Laboratory Instruction

LEARNING OBJECTIVES

The objectives of this experiment are to . . .

- understand the titration curves for the following solutions
- a weak acid: acetic acid, CH_3 COOH.
- a strong acid: hydrochloric acid, HCl.
- an acidic commercial cleanser.
- a basic commercial cleanser.
- use the titration curves to calculate the percent of the active ingredients in the commercial cleansers.
- determine the K_a of a weak acid.

BACKGROUND

A plot of the pH of a solution against the volume of "titrant" added is called a titration curve. The pH can be measured directly with a pH meter while titrant is added from a buret. For the acids used in this experiment the titrant will always be a 0.1 M solution of the strong base NaOH. From the form of the titration curve it can be determined whether the solution consists of a strong or weak acid. Furthermore, if it is a weak acid, the equilibrium constant for its dissociation can be calculated.

Strong acids

For a strong acid HA, the equilibrium constant K_a for the process

$$HA + H_2O \leftrightarrows H_3O^+ + A^- \qquad (1)$$

is so large that it is completely dissociated into H_3O^+ and A^- at usual concentrations, and hence the H_3O^+ concentration simply equals the acid concentration which remains unreacted by the NaOH. This is true until the titration has reduced the concentration of HA to less than 10^{-6} *M*. At this point the dissociation of water according to the equation

$$H_2O + H_2O \leftrightarrows H_3O^+ + OH^- \qquad (2)$$

$$K_w = [H_3O^+]\,[OH^-] = 10^{-14} \qquad (3)$$

begins to govern the H_3O^+ concentration. At the exact equivalence point (where the moles of base added equal the initial moles of acid present), the H_3O^+ concentration comes entirely from this source and is therefore equal to 10^{-7} and the pH is seven.

Weak acids

For a weak acid the equilibrium constant for reaction (1) is small (between 10^{-2} and 10^{-7}), so that the concentration of $[H_3O^+]$ and hence the pH is governed by Ka.

$$K_a = [H_3O^+] [A^-] / [HA] \qquad (4)$$

The titration curve that you obtain should be considerably different from that obtained when the same concentration of strong acid is titrated. Obviously the $[H_3O^+]$ concentration will be lower (and the pH therefore higher) throughout the titration because not all of the acid is dissociated. You should also find that the shape of the curve is somewhat different. The reason for this will become clear if the following three points along the titration curve are considered in some detail.

(a) **Zero titrant.** Since the dominant source of $[H_3O^+]$ is the acid dissociation described by equation (1), $[H_3O^+] = [A^-]$ from the stoichiometry of the equation. Therefore equation (4) reduces to

$$K_a [HA] = [H_3O^+]^2 \qquad (5)$$

If we further assume that [HA] is given by the acid nominal molarity of the solution, then the $[H_3O^+]$ concentration and hence the pH can be calculated if K_a is known. K_a is most conveniently obtained from the following point on the titration curve.

(b) **Halfway to the equivalence point.** At this point half of the acid has been titrated, and hence $[A^-] = [HA]$. Therefore, equation (4) reduces to the simple expression

$$K_a = [H_3O+] \quad \text{or} \quad pK_a = pH \qquad (6)$$

This is a rather remarkable point on titration curves since the pH is determined by the value of pK_a (log K_a) and is independent of the initial acid concentration and any subsequent dilution.

To determine the pK_a of a weak acid, we need to locate this half-equivalent point accurately, and this can be done by first finding the following point on the titration curve.

(c) **The equivalence point.** When the monoprotic acid has been completely titrated by addition of an equal number of moles of base, we have reached the equivalence point. On the titration curve this will appear as the point of maximum slope. If the data are obtained by adding equal amounts of titrant throughout, the equivalence point will probably be very poorly located because there will be a sudden jump between two points. We therefore attempt to add small amounts of titrant in the vicinity of the equivalence point and thus accurately determine the point of inflection. Once this has been determined, the half way point can be calculated and pKa determined as discussed in part (b). Let us now consider the calculation of the exact pH at the equivalence point.

The solution contains an amount of A equal to the original acid present, but in a volume which is larger by an amount depending on how much titrant was added. The concentration of A is then easily calculated by considering the dilution factor. To calculate the pH at this point, we consider the following equilibrium in which A is said to be hydrolyzed:

$$A^- + H_2O \; <==> \; HA + OH- \qquad (7)$$

It is not difficult to show that K_h for reaction (7) is related to K_a and K_w by multiplying both numerator and denominator of the Kh equation by $[H^+]$, and rearrange, as follows:

$$K_b = \frac{[HA][OH^-][H^+]}{[A^-][H^+]} = \frac{[HA]}{[A^-][H^+]} \times \frac{[H^+][OH^-]}{} = \frac{K_w}{K_a} \qquad (8)$$

From the stoichiometry of equation (7), $[HA] = [OH^-]$ and equation (8) can be written

$$K_b = \frac{[OH^-]^2}{[A^-]} \qquad (9)$$

When K_a is obtained from part (b), K_b can be calculated with equation (8) ($K_w = 10^{-14}$). Then $[OH^-]$ and pOH can be calculated using equation (9). The pH at the equivalence point is then given by (14 – pOH).

Acid-Base titration of commercial cleansers

Potentiometric titration can be applied to the determination of acidic and basic compounds in household cleansers. The cleansers generally contain one or two acids or bases and their concentrations can be determined from the one or two equivalence points on the titration curves. The acidic household cleansers usually contain hydrochloric acid, phosphoric acid, sodium bisulfate, or hydroxyacetic acid, which remove alkaline scale deposits and stains. The basic cleansers usually contain ammonium hydroxide, sodium hydroxide, sodium hypochlorite or sodium carbonate. The weaker bases cut grease while the stronger bases and oxidizing agents dissolve animal matter such as hair, grease, and foodstuffs.

Lysol® (Reckitt Benckiser (UK) Limited) is an acidic cleanser, containing hydrochloric acid as an active ingredient. The percentage content of HCl can be calculated from the titration data.

Liquid Plumr® (The Clorox Company) is a two component basic cleanser containing sodium hydroxide and sodium hypochlorite (NaOCl). Sodium hypochlorite is an oxidizing agent as well as a weak base and, together with sodium hydroxide, is used as a drain cleaner.

The titration of a base with a strong acid is just the reverse of the titration of an acid with a strong base. The student will find it easy to grasp what happens during the titration of a mixture of strong and weak bases if he/she considers the following two points along the curve.

(a) **Zero titrant.** The strong base will be completely dissociated, giving an equivalent OH^- concentration. The weak base will be only partially dissociated and make a much smaller contribution to the total $[OH^-]$ present. The presence of OH^- from the strong base will, in fact, suppress the dissociation of the weak base, since the equilibrium

$$B^- + H_2O \Rightarrow BH + OH^- \qquad (10)$$

will be shifted to the left. Thus, the first equivalence point gives the volume of the titrant reacting with the strong base.

(b) **When strong base has been titrated.** At this point we simply have a solution of the weak base that has been diluted. The difference between the first and the second equivalence points gives the volume of strong acid required to react with the weak base.

SAFETY PRECAUTIONS

Safety goggles must be worn in the lab at all times. Any skin contacted by chemicals should be washed immediately.

BEFORE PERFORMING THIS EXPERIMENT . . .

... you will need *one* of the following *MicroLAB* programs.

- **pH.vs.Kbd** experiment: Sends the total volume of titrant (the solution in the buret) added to the analyte (the solution in the beaker) to the **Graph** view X Axis, the **Digital Display** view, and a **Spreadsheet** column, and (2) sends the pH value resulting from the latest addition of titrant to the Y Axis of the **Graph** view, the **Digital Display** view, and a second, corresponding **Spreadsheet** column. This program is suitable for a manual titration in which you will manually add small volumes of titrant to your analyte solution and input each buret reading into the computer.
- **pH.vs.Time** experiment: a program that sends *time* and pH to the spreadsheet file every ½ second. After the titration is complete, you can use the **Spreadsheet** to convert the time into a volume. To do this, however, you need a constant flow buret. This can be accomplished by first adjusting the flow of your buret to deliver 1of solution in about 8 seconds, then swinging the buret into the titration beaker. During the titration, keep adding the NaOH to the buret so that the buret level is in the same volume range as when you measured the flow rate. To convert the time into the volume of NaOH added, the time data in the **Spreadsheet** should be divided by the flow rate (in sec/ml). Although this technique takes a little bit more finesse, the results are normally very good and require much less time than the "manual" method described in the previous paragraph. You will decide which method of titrating is best for you.

Interpreting the pH titration curve

An example of a pH titration curve obtained using the lab interface is shown in Figure 1. A strong base (NaOH) was added to a strong acid (HCl). The equivalence point is the point at which the pH versus volume curve is the steepest. The curve shown in Figure 1 was obtained with as a drop counter titration, obtaining 356 data points in less than five minutes, then the drops converted to volume. If you do a manual titration, you will have far fewer data points.

The **Spreadsheet** makes it easy to find the equivalence point of a titration curve. Since the equivalence point is the steepest point of the curve, taking the derivative of the curve will make the equivalence point readily apparent. Click on **Plot a Derivative** function in the **Analysis** option and select pH vs. Volume. Figure 2 shows an example of what the derivative looks like when superimposed on the titration curve from Figure 1.

EXPERIMENTAL PROCEDURE

Preparation of NaOH for the titration of the acids

The sodium hydroxide solution supplied is about 2.5 *M*. Using a graduated cylinder, measure 10 ml of 2.5 *M* NaOH into a 250volumetric flask. Make up to the mark with de-ionized water and mix well. Rinse and fill the buret with this dilute solution of NaOH.

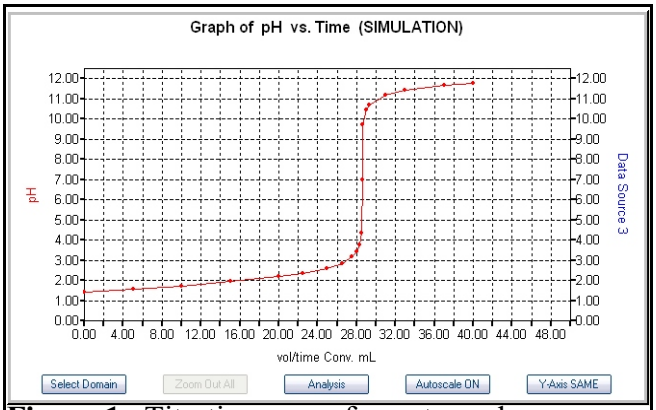

Figure 1. Titration curve for a strong base versus a strong acid.

Calibrating the pH probe

1. The pH probe is a delicate, complicated sensor comprised of an ion-sensitive glass tip, metal electrodes, and chemical solutions sealed in a glass or plastic tube. Be careful not to drop the pH electrode or hit it with the stirring rod. Gently rinse the glass tip with de-ionized water before moving the electrode from one solution to another. Once you are finished using the electrode, always return it to the storage beaker.

2. Click on **pH** in the **Variables View** and recalibrate your probe with the pH 4, 7 and 10 buffers supplied. Be sure to rinse the pH probe with distilled water after each buffer and before you place it in your analyte solution. Between titrations, the probe should be stored in the pH 7 buffer, then rinsed well with distilled water before inserting into your titration beaker.

Titration of the acids

1. All the acids supplied will be about 0.1 *M*. Using a pipet, measure 25.00of HCl into a 250beaker. Add 100of H_2O and five drops phenolphthalein. Be sure to record the concentration of HCl, since it will be used to calculate the concentration of your NaOH solution.

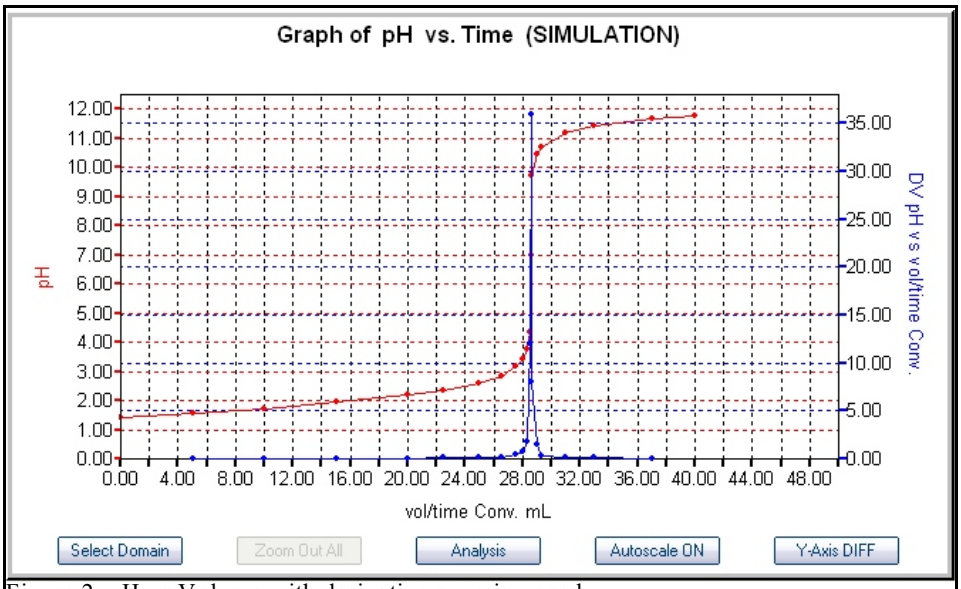

Figure 2. pH vs Volume with derivative superimposed.

Note: Do either step 2a *or* 2b. Do *NOT* do both!

2. (a) **Using a pH titration program designed for a "manual" titration**, (**pH.vs.Kbd** experiment), titrate the sample with the NaOH solution. Remember to measure the pH of the solution with respect to the volume of NaOH added. In the beginning, add NaOH in 1increments. As the pH begins to rise significantly, use 0.5increments or less. As you approach the equivalence point (indicated by a more persistent pink color from the phenolphthalein), the smaller the increment, the better (~0.05 ml, or one drop). **Once the end point has been reached with the indicator,** note the volume of base added and continue the titration at the one-drop volume increment for a least an additional five drops. Then gradually increase the volume increments (up to a maximum of 1.0 ml) until you have added approximately 10 ml of NaOH beyond the end point. For a good titration curve, you will want at least 30 data points. A timed titration is likely to give you 10 times as many points!

2b. **Using a pH titration program designed for an "automatic" or "timed" titration**, (**pH.vs.Time** experiment). Before beginning the titration, make sure you have adjusted the flow rate of the buret to two to four seconds per drop, for example between the 2 and 3 ml marks, with the flow dropping into a waste beaker.

2c. Then, with the buret full and still flowing, place your beaker under the buret and

simultaneously start your program to begin taking data. It is now critical to keep the liquid level of the buret at the same level as that which you measured the flow rate, using the titrant in the plastic wash bottle. Depending upon the exact flow rate, the titration will take between four and seven minutes. Watch for the color end point and take data for at least two minutes beyond this point.

3. Using a graduated cylinder, measure 25of 0.1 *M* acetic acid (CH_3COOH) into a 250 ml beaker. Add 50.0of water and 5 drops phenolphthalein.

4. Titrate the acetic acid with strong base as directed above for HCL.

Titration of Lysol

Weigh a 150beaker on the analytical balance. Dispense 1of Lysol into the beaker. **Caution: handle Lysol with care - strongly acidic.** Reweigh the beaker on analytical balance. Add 60of water. Repeat step 2 above, the NaOH supplied is 0.100 M

Titration of Liquid Plumr

Weigh a 150beaker on analytical balance. Dispense 2of Liquid Plumr into the beaker. **Caution: handle Liquid Plumr with care - strongly basic.** Reweigh the beaker on analytical balance. Add 60of water. The HCl solution supplied is 0.100 *M*. Rinse and fill the buret with this solution. Repeat step 2 above. Continue the titration to a pH near 2. Your data should show two inflections.

DATA ANALYSIS

1. Using the **Spreadsheet**, plot the pH versus volume data. Use the **Analysis** option to find the derivative of the curve and plot the pH on **Y1-axis**, the volume of NaOH added on the **X-axis,** and the derivative of the pH-volume curve on **Y2-axis**. Remember, if you did a "timed" titration, you will have to use the **Analysis** option to convert time into volume using your flow rate. Obtain a printout of your plot. **DO NOT PRINT DATA TABLES, they are too long.**

2. Using your titration curves and derivative plots, determine the equivalence points for all the titrations. Calculate the exact molarity of the NaOH solution using the HCl titration data.

3. Determine the half-equivalence point for the titration of acetic acid and use it to determine its K_a value. Compare the K_a with the accepted value for acetic acid, 1.8×10^{-5}.

4. For the Lysol, determine the equivalence point and calculate the percentage content of HCl. Use the exact concentration of the NaOH solution calculated in (2) above.

5. For the Liquid Plumr, determine where the two equivalence points are and then record the pH and volume of the HCl at both the first and second equivalence points. Calculate the percentage content of both the NaOH and NaOCl in Liquid Plumr.