

Potentiometric Titration of an Unknown Weak Monoprotic Acid

East Stroudsburg University

Chemistry 371

Fall, 2008

Introduction

The purpose of this experiment is to perform a potentiometric titration of an acid using a glass electrode and a pH meter. The potential that develops across the glass membrane of the electrode is proportional to the concentration (more exactly, the *activity*) of H^+ in solution. In this laboratory, you will be given a sample of a weak acid, and with information obtained from your titration curve, you will be able to calculate the molecular weight and the pK_a of the unknown. This should allow you to identify the unknown, and to calculate a theoretical titration curve which you can match to your experimental result.

The dissociation of a weak acid (represented by HA) in water can be described by



where H^+ represents the acidic proton and A^- represents the conjugate base of the weak acid. The equilibrium constant for the dissociation is given by K_a which can be expressed as

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

This equation can be rearranged in terms of $[H^+]$

$$[H^+] = \frac{K_a [HA]}{[A^-]}$$

At a volume of titrant equal to half that required to completely neutralize the weak acid present, the remaining concentration of HA will be equal to that of A^- formed during the neutralization reaction.

$$[HA] = [A^-]$$

and

$$[H^+] = K_a$$

By converting $[H^+]$ to pH, a useful relationship between the pH at the midpoint of the titration and the pK_a is obtained

$$pH = -\log [H^+] = -\log K_a = pK_a$$

Procedure

You will be given an unknown sample, and you should ask the instructor the maximum sample size to weigh out. Weigh the sample by difference into a clean 100 mL beaker and dissolve it with about 50 mL of H₂O. If the sample appears to be insoluble, start again with a clean beaker and add the minimum amount of ethanol needed to dissolve, then add 50 mL of H₂O. Quantitatively transfer the dissolved sample to a clean 200.00 mL volumetric flask and dilute to the mark. Mix thoroughly. When the actual titration is to begin, pipette 25.00 mL of H₂O (unless you have solubility problems, in which case you should use either ethanol or a water/ethanol mixture) and 50.00 mL of the sample solution (only 1/4 of the total mass!) into a 150 mL beaker.

Make sure you understand the operation of the particular pH meter you will use for your measurements. Standardize the pH electrode using pH 4.00 and pH 7.00 standard buffer solutions. Place a stir bar in the bottom of the beaker containing the unknown, and the beaker on the stir plate. Place the pH electrode into the solution, taking care that it is well away from the stirring magnet (which should stay in the center of the beaker). Run the stirring magnet at a slow speed throughout the titration. You will be measuring pH as a function of standard NaOH solution (prepared and standardized previously) added from a 50.00 mL buret (Class A tolerance). The most helpful information in the identification of your unknown will occur in those regions where the pH changes are great for small aliquots of base. Therefore, in these regions you should collect more data points than in the “buffer” regions.

It is advisable to titrate one sample quickly in one- or two-mL steps, taking the pH reading after it becomes stable (generally no more than 30 seconds). Prepare a table in which you record your data, with columns for “titrant added” and “pH”. Read the buret and the pH meter to two decimal places. This “quickie” will allow you to find the endpoint region, and to be prepared for its arrival during the next titration.

Repeat the process of pipetting 25.00 mL of H₂O and 50.00 mL of sample solution. Do a second titration, being careful to take enough points to define the endpoint well. When the change in pH value upon addition of 1-mL of titrant exceeds 0.10 pH units, start adding 0.5-mL aliquots, and read the buret and the pH meter as accurately as possible. When the change exceeds 0.10 pH units each time an aliquot is added, start adding 0.1-mL aliquots (or smaller with “split drops”). When the endpoint is passed, continue to add titrant, gradually increasing the size of each aliquot added up to 1.0 - 2.0 mL. Continue titrating until the pH is well above 10 - 11.

Results

Plot your titration curve using a program like Excel. Since mL added is the independent variable, it goes on the x-axis. Next, calculate and plot the first derivative of your data, which usually is peak-shaped, and gives the endpoint as the maximum value. The moles of titrant used to reach the endpoint will be equal to the moles of unknown acid in the solution titrated. Use this information to calculate the molecular weight of the unknown. Since $\text{pH} = \text{pK}_a$ at a volume of titrant corresponding to half of the endpoint volume, you may easily calculate the K_a for your unknown.

Your unknown is one of the compounds in the following list. Once you have identified it, use its actual value for K_a and calculate a theoretical titration curve. This should have pH values that are calculated for each of the following: initial pH for the concentration of unknown you started with; pH at 1/4, 1/2, and 3/4 of the way to the endpoint; pH at equivalence point; at least two points past the equivalence point. Plot the actual titration curve on the same page as the theoretical curve for an easy comparison. If the two do not match very well, you may need to choose another possibility for the identity of your unknown.

Turn in these plot(s) with your report, and include all of your calculations. In the discussion section, give all the reasoning you used to identify the unknown. Ideal titration curves will not be obtained in all cases but enough information will be available to complete the experiment successfully. You may wish to look for outside confirmation such as information in textbooks, Merck index, CRC, etc. For example, some of your materials will be granular or flakes, colored or colorless, very soluble in water or fairly insoluble. This type of information may help you choose between more than one likely candidate. Be sure to include this information in your discussion.

Data for Acid Unknowns

Name	Formula	pK _a Value	Formula Weight
acetic acid	HC ₂ H ₃ O ₂	4.74	60.05
anilinium hydrochloride	C ₆ H ₅ NH ₃ ⁺ Cl ⁻	4.60	129.59
benzoic acid	C ₆ H ₅ COOH	4.20	122.12
boric acid	H ₃ BO ₃	9.24	61.84
chloroacetic acid	ClCH ₂ COOH	2.82	94.50
<i>m</i> -chlorobenzoic acid	ClC ₆ H ₄ CO ₂ H	3.82	156.6
<i>o</i> -chlorobenzoic acid	ClC ₆ H ₄ CO ₂ H	2.92	156.6
<i>p</i> -hydroxybenzoic acid	HOC ₆ H ₄ CO ₂ H	4.58	138.12
hydroxylammonium hydrochloride	HONH ₃ ⁺ Cl ⁻	5.96	69.49
mandelic acid	C ₆ H ₅ CH(OH)CO ₂ H	3.40	152.15
<i>m</i> -nitrobenzoic acid	O ₂ NC ₆ H ₄ CO ₂ H	3.50	167.12
<i>p</i> -nitrobenzoic acid	O ₂ NC ₆ H ₄ CO ₂ H	3.44	167.12
potassium bitartrate	KHC ₄ H ₄ O ₆	4.54	188.18
potassium hydrogen phthalate	KHC ₈ H ₄ O ₄	5.41	204.23
salicylic acid	HC ₇ H ₅ O ₃	2.98	138.1
sodium bicarbonate	NaHCO ₃	10.36	84.01
sodium citrate, dibasic	Na ₂ HC ₆ H ₅ O ₇	6.40	236.1
sodium malonate	NaHC ₃ H ₂ O ₄	5.66	126.1
sodium phosphate, dibasic	Na ₂ HPO ₄	12.32	143.0