University of Wisconsin
Chemistry 116
Study of an Unknown Diprotic Weak Acid[i]

In this laboratory activity you will study the equilibrium of a diprotic weak acid by experimentally determining a titration curve for an unknown diprotic weak acid solution and comparing your experimental curve to a mathematical model based on a systematic treatment of the equilibrium system.

The experiment has three parts:
1.   Preparation of standard base solution.
2.   One rough and one careful potentiometric titration on an unknown diprotic acid to get the experimental titration curve.
3.   Mathematical modeling of the diprotic acid equilibrium and a fit of your experimental data to theoretical models.

Preparation and Standardization of Standard 0.1 M Standard NaOH Solution

From the NaOH solution provided in the lab, prepare 500 mL of a solution that is approximately 0.1 M NaOH. Insure thorough mixing of this solution and store this solution in a plastic bottle.

Since this concentration is only approximate, it will be necessary to standardize this solution. This may be done by titrating potassium acid phthalate ($KHC_8H_4O_4$, abbreviated KHP, gram-molecular weight 204.2) with the approximate 0.1 M NaOH solution. KHP is an excellent primary standard because it is easily obtained in very pure form, has a high molecular weight, and is non-hygroscopic. Since the KHP can be measured very carefully, the concentration of the NaOH solution may be measured very accurately.

To perform this titration, calculate the weight, in grams, of potassium acid phthalate which would be required to neutralize 25.00 mL of 0.1 M NaOH solution. Add the KHP to a clean Erlenmeyer flask. Dissolve this material in 25-50 mL of distilled water.

Add 2-3 drops of phenolphthalein indicator to the flask containing the KHP solution. Place a small Teflon™ coated magnet into the flask containing the KHP solution, and place this flask on the stirring/hot plate. Turn on the stirrer to a medium setting. While stirring the KHP solution, add the dilute NaOH solution from the buret to the flask. Remember that this titration should take about 25 mL to for neutralization to occur, so most of that amount may be added rather quickly. Add the last 4-5 mL slowly and note when you observe a faint color change which remains visible for about 1 minute in the solution in the flask and record how many mL of NaOH were required to bring about this change.

Repeat the titration 2 more times for a total of 3 accurate titrations. (Molarities should agree within 2%). Calculate the concentration of the standardized NaOH solution you have prepared.

Potentiometric Titration

Obtain a sample of the unknown weak acid from your laboratory instructor. Weigh accurately approximately 1.5 grams of the weak acid and quantitatively transfer to a 250 mL volumetric flask. Dissolve and dilute to the mark with deionized water.

For the rough titration, titrate 50.00 mL of the acid solution by adding 1.00 mL portions of your base while monitoring the pH with a pH meter. Titrate until the pH is 12.0. Make a plot of pH versus volume of titrant added. Identify the regions on this curve where the slope is large.

For the careful titration, again use 50.00 mL of the weak acid solution, bit this time titrate dropwise through the regions of large slope. Read the buret volume after the addition of each drop. You may still titrate the solution with 1.00 mL additions in the regions of small slope. Plot the potentiometric titration curve for the weak acid.

From your titration data, calculate the concentration of your weak acid solution and the molecular weight of the weak acid. Get approximate values of the pK_as for the diprotic acid.

Modeling of a Diprotic Acid Solution

To model the titration curve, you will use appropriate equations[ii] from a systematic approach to the equilibrium of a mixture of a diprotic acid solution and a strong base solution. Set up the equations for the α fraction for each of the weak acid components at a given pH. Begin with your estimated values of the two pK_a constants, but recognize that these will be "tweaked" to obtain a good fit to the experimental titration curve. For a diprotic acid:

$$\alpha_{H_2A} = \frac{[H^+]^2}{[H^+]^2 + [H^+] \cdot K_{a1} + K_{a1} \cdot K_{a2}} \qquad \alpha_{HA^-} = \frac{[H^+] \cdot K_{a1}}{[H^+]^2 + [H^+] \cdot K_{a1} + K_{a1} \cdot K_{a2}}$$

$$\alpha_{A^{2-}} = \frac{K_{a1} \cdot K_{a2}}{[H^+]^2 + [H^+] \cdot K_{a1} + K_{a1} \cdot K_{a2}}$$

Plot the alpha fractions as a function of pH. Think about how the alpha plots relate to the important regions of your pH titration curve.

Now use the charge balance equation: $[Na^+] + [H^+] = [OH^-] + [HA^-] + 2[A^{2-}]$ to calculate the volume of NaOH added at a given pH. Be careful here as you must include the dilution of the acid and the base. You also need to use your experimentally determined weak acid concentration to convert the α fractions to actual concentrations.

On the same axis, plot your theoretical values and your experimental values of pH vs V_b added. Tweak your values of pK_{a1} and pK_{a2} until you get the best "visual" fit of your experimental data. You may also need to include your weak acid concentration as a fitting parameter in order to obtain a reasonable fit.

Finally, correct your model to include activity. To include activity, first calculate the ionic strength, μ, of the solution in your uncorrected model from:

$$\mu = \frac{1}{2}\sum_i c_i z_i^2$$ where c is the concentration of each ionic species and z is its charge. Then use the Davies equation, which is an approximation of the extended Debye Huckel equation to calculate the activity coefficient, γ, for each species.

Davies Equation: $$-\log\gamma = 0.51z^2\left[\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.3\mu\right]$$

Now use the activity, $a_i = \gamma_i \cdot c_i$, in your model. Note that the pH meter also reads activity, pH = - log (a_H^+), and $K_w = (a_H^+)\cdot(a_{OH}^-)$.

Repeat your plot of the theoretical and experimental titration curves. Re-tweak your values of pK_{a1} and pK_{a2} until you get the best "visual" fit of your experimental data. Compare the values for the corrected and uncorrected models. Ask the TA for the identity of your weak acid and compare your pK_{a1}, pK_{a2}, and molecular weight to literature values. If there is a difference, which model gives you a better result as compared to the literature.

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[i] This experiment is a modified version of an experiment used in Chem327/329 analytical courses at the University of Wisconsin-Madison. Modifications were made by R. McClain in April of 2009.

[ii] Harris, Daniel C., **Quantitative Chemical Analysis, 6th Ed.** W.H Freeman and Co. New York, 2003.