CHEM 322: DETERMINATION OF pK_a VALUES OF WEAK ACIDS

The dissociation of a weak acid can be described by the equation $HA \rightleftarrows H^+ + A^-$

and the equilibrium constant for this reaction by $K_a = [H^+][A^-] / [HA]$.

The ionization constant K_a is an intrinsic property of a given weak acid/conjugate base pair which describes the "stickiness" of the conjugate base for the H^+ (the tenacity with which it holds on to the proton).

If we take the logarithm of all terms, the latter equation can be written $\log K_a = \log[H^+] + \log([A^-]/[HA])$

and rearranged to $-\log[H^+] = -\log K_a + \log([A^-]/[HA])$

Since the mathematical operator "p" means "take the negative log of", we can finally write

$$pH = pK_a + \log([A^-]/[HA]) .$$

Consideration of this equation reveals a couple of interesting facts.

First, if $[A^-] = [HA]$, then their concentration ratio is exactly 1.00, and the log of 1.00 is zero. Under this condition, $pH = pK_a$. Thus, if the experimenter arranges for the concentrations of the weak acid and its conjugate base to be identical, then the pH of the solution will exactly equal the pK_a of the weak acid.

Second, it is evident that any given ratio of concentrations of conjugate base to parent weak acid will specify a unique value of pH in the solution. Alternatively, setting the pH of a solution that contains a weak acid and its conjugate base will dictate a particular ratio of concentrations of these two species. Either way, the pK_a value is what governs the outcome.

The structure of a weak acid has a lot to do with how strongly it holds on to its proton. If the proton is NOT held tightly (shown by a large K_a [low pK_a]), the acid ionizes easily and is relatively strong. Conversely, if the proton IS held tightly (shown by a small K_a [high pK_a]), the acid is difficult to ionize and is relatively weak. This experiment is designed to help you explore the *measurement of pK_a values of weak acids and bases can test predictions about how certain structural modifications should affect their relative strengths.*

pK_a values are easy to measure by titration. One does not need to know the starting concentration of either the weak acid or the strong base used to titrate it. All that is necessary is careful recording of the pH of the solution as a function of volume of base used during the titration, and accurate determination of the end point. There are some practical considerations which are detailed below.

EXPERIMENTAL SECTION

It's wise to arrange things so that we (a) don't use a lot of materials and (b) work with convenient volumes. Titration of roughly 0.003 mole (3 millimoles) of weak acid works well. If the acid has a formula weight of about 100 g/mole, this works out to about 0.3 g. If you're using a solid acid, you'll need to weigh about this much. If you're working with a liquid, this is an amount that occupies a volume of roughly 300 microliters (0.3 mL) - about 6-8 drops from a Pasteur pipet. Actual amounts are not critical as long as they are somewhat close to these values. Put the acid you select in a 250 mL Erlenmeyer flask and add about 10 mL of ethanol. Swirl to disslove as much as possible. Now slowly and with good swirling add 40 mL of DI water. Some acids may precipitate, but don't worry – this will not affect your results, and all of the acid will eventually dissolve by the end of the titration. Prepare three separate samples of each acid you plan to titrate.

The base for titration (NaOH) should be at such a concentration that you will use about 2/3 of a 50 mL buret's capacity – about 30 mL. (Why? [a] You don't want to use a small volume, because then your volume measurement will be more uncertain. [b] You don't want to use much more than 30 mL, because then you risk needing to refill the buret.) The stoichiometry is one NaOH consumed for each ionized proton. Thus, a convenient concentration for the NaOH (assuming a monoprotic acid – one that can lose only one proton) would be 0.003 mole/0.03 L = 0.1 M. Any concentration that is close to this would be fine – if the NaOH is more concentrated, you'd use less of it, and if less concentrated, you'd use more. You may have to dilute a more concentrated solution of NaOH from the lab to get your 0.1 M stock solution. Be sure to make enough – you'll need to do at least 6 titrations (3 for each of two different acids).

Get a buret and fill it with water, then allow it to drain and watch to see that water does not bead on the walls. Clean if necessary using Alconox solution and a buret brush and then rinse many times with DI water. Use a little of your NaOH solution to rinse the buret (be sure no water is left to dilute your NaOH and that all air bubbles have been expelled from the valve and tip). Fill the buret with your NaOH and invert a small beaker over the open top.

Obtain a pH meter and combination pH electrode. Standardize the meter and electrode using the provided pH 10 and 7 buffers according to instructions on the meter. Ask for help if you are not sure how to do this. It is important to keep the electrode moving in the standardizing solution until the instrument "locks in" the reading. Rinse the electrode copiously into a waste beaker between readings.

Magnetically stir your dissolved acid sample, and obtain the temperature of your sample. You'll want to defeat the pH meter's "AutoLock" feature if it has one (ask how). Record the initial pH reading, then run in about 1 mL of base, allow the reading to stabilize, and record both volume and pH. Continue addition of small volumes of base and recording of pH until the pH starts to rise rapidly. This is the time for careful work. It's really important to rinse down the sides of the flask with your wash bottle to be sure all the acid will be titrated. You may want to ask for advice. Add smaller and smaller volumes of base as the pH rises more and more rapidly with each addition. At the end you'll want to add one drop at a time. The titration is complete when the pH passes about 8.5. This is the endpoint. The rapid rise in pH caused by adding a tiny volume of base signals that no more HA remains to donate H^+. Ideally, you would like to get the volume reading when the pH is about 8.5, but this will be nearly impossible. Repeat this process for all samples.

ANALYSIS OF DATA

The equation **$pH = pK_a + \log([A^-]/[HA])$** is linear since it has the form **$y = mx + b$** , where y = pH, m = 1, and x = log([A-]/[HA]). If you plot **pH** *(y axis)* against **log([A-]/[HA])** *(x axis)*, the points should follow a straight line which has a y-intercept equal to pK_a. The problem is how to figure out values for A- and HA.

Let HA_0 be the amount of acid you added to the flask, A- the amount of acid that has lost its proton, and HA the amount remaining un-titrated at any point in the titration. Then at any point in the titration, A- + HA = HA_0. The volume of NaOH *at the endpoint* (call it V_{max}) is directly related to HA_0 (recall the stoichiometry). The volume of NaOH used at any other point during the titration (call it V) is directly related to A-, because each NaOH consumes one HA and produces one A-. Thus, since HA = HA_0 – A-, we can replace HA with (V_{max} – V). Combining these relationships, it's evident that a plot of pH against log[V/(V_{max} – V)] should produce the desired plot. Note that you can't use V_{max} as one of your data points – it can only be used to compute (V_{max} – V).

LAB REPORT

Introduction:

- What are the major objectives of this experiment?
- Explain why data are presented in the manner chosen.
- Show acid – base reactions (including pertinent resonance structures) as figures.

Results:

- Present a plot for each data set (*please DON'T list the raw data, unless it is included in the appendix)* and report the pK_a for each acid as the average of the three values you found. **Use figure guidelines as established in CHEM 321 (posted on CHEM 322 course website).**

Discussion:

- Restate objectives and related theory (both structures vs. pKa and data analysis rationale).
- Compare your experimental pKa results to the published pKa values of your acids. Discuss the quality and precision of the data (any outliers? nonlinear?).
- Comment on the relationship between structure and pK_a (don't forget to consider possible resonance structures of both the acid and its anion, and how each would affect the relative stability of the acid or anion compared to those of the other acid you tested).
- If your experimental pKa values did not match published pKa values, speculate on why. (Note: human error is usually *not* the reason behind this difference).