A Simplified Method for Finding the pK_a of an Acid–Base Indicator by Spectrophotometry

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General chemistry textbooks devote much space to the important concept of equilibrium. To illustrate one aspect of equilibrium, a new laboratory experiment on the measurement of an equilibrium constant was desired. Ideally, the experiment would

1. result in a reasonably accurate value of the equilibrium constant,

2. use a small number of solutions that are safe to handle—or at least be familiar to students—and simple to dispose,

3. use equipment commonly found in a general chemistry laboratory, and

4. not exceed the skills of a typical general chemistry student.

A well-known experiment in analytical and physical chemistry laboratory courses is the spectrophotometric determination of the pK_a of an acid–base indicator (1–9). Following published procedures, this experiment yields accurate results using equipment found in most general chemistry labs (pH meters and single-wavelength spectrophotometers, such as the Spectronic 20). The acidic and basic solutions generated during the experiment are probably familiar to students and can be disposed by neutralizing them then pouring them down the drain. In most published procedures, however, several buffer solutions must be prepared by technicians before the lab or by students during the lab. Also, the procedures would be difficult for most general chemistry students to complete in a three-hour laboratory period. We have developed a simpler method that uses fewer solutions; pK_a results for this method using eight common indicators are reported here.

For the simple method outlined here to work well, there must be only one acid form of the indicator (HIn) and one base form (In⁻) in equilibrium:
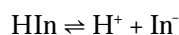
$$HIn \rightleftharpoons H^+ + In^-$$

If we use concentrations rather than activities, the expression for the equilibrium constant for the reaction is

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

The logarithmic form of the equation is

$$pK_a = pH + \log_{10}\frac{[HIn]}{[In^-]} \tag{1}$$

The acid form of the indicator has a color, such as yellow, with its corresponding λ_{max} at one wavelength, and the base form has another color, such as blue, with its corresponding

λ_{max} at a different wavelength. If the cell path length is kept constant and all solutions contain the same total molarity of indicator, the acid–base ratio at the λ_{max} of either the acid or base form is given by (3, 10, 11)

$$\frac{[HIn]}{[In^-]} = \frac{A - A_{In^-}}{A_{HIn} - A} \tag{2}$$

where A is the absorbance of the solution containing a certain total concentration of the acid–base mixture, A_{In^-} is the absorbance of the base form at the same concentration, and A_{HIn} is the absorbance of the acid form at the same concentration.

Substituting the expression for the HIn–In⁻ ratio from eq 2 into eq 1,

$$pK_a = pH + \log_{10}\left(\frac{A - A_{In^-}}{A_{HIn} - A}\right) \tag{3}$$

or

$$\log_{10}\left(\frac{A - A_{In^-}}{A_{HIn} - A}\right) = pK_a - pH \tag{4}$$

The pK_a of an indicator can be determined by either of two equivalent methods, an algebraic method or a graphical method. In the algebraic method, sets of pH and absorbance values are substituted into eq 3 and the pK_a is calculated for each set. The pK_a reported is the average of the calculated pK_a's. In the graphical method, $\log_{10}[(A - A_{In^-})/(A_{HIn} - A)]$ vs pH from eq 4 is plotted, and pK_a is obtained as the x-intercept. The line should have a slope of –1.

Experimental Procedure

A 1% solution of phenolphthalein in isopropanol, pHydrion buffer capsules (pH 4, 7, and 10), and 50% sodium hydroxide solution were purchased from Fisher Scientific Co. Aqueous solutions containing 0.04% bromocresol green, 0.04% bromocresol purple, 0.04% bromophenol blue, 0.04% bromothymol blue, 0.10% methyl orange, 0.10% sodium salt of methyl red, and 0.04% phenol red were obtained from Aldrich Chemical Co.

The procedure for determining the pK_a for bromophenol blue is described in detail. Conditions for determining the pK_a values for the other indicators are tabulated.

A bromophenol blue solution in its base form was prepared by dissolving 6 drops of the 0.04% dye solution and 2 drops of 1 M NaOH in 10 mL of distilled water. To obtain an estimate of λ_{max}, the absorbances of the solution were measured on a Bausch & Lomb Spectronic 20D spectrophotometer at 20-nm intervals from 560 to 640 nm (Table 1). The absorbance

Table 1. Absorbance Values for Bromophenol Blue

Wavelength/nm	Absorbance
560	0.553
580	0.812
600	0.796
620	0.281
640	0.077
590	0.914

Table 2. Conditions for Obtaining λ_{max} for Indicators

Indicator	No. of Drops		Wavelength/nm		
	Dye Soln	Base or Acid	Range	λ_{max} Lit (12)	λ_{max} Exptl
Bromocresol green	9	2[a]	580–660	617	615
Bromocresol purple	9	2[a]	540–620	591	590
Bromophenol blue	6	2[a]	560–640	592	590
Bromothymol blue	9	2[a]	580–660	617	615
Methyl orange	1	2[b]	460–540	522	505–510
Methyl red	1	2[b]	480–560	530	520–525
Phenolphthalein	1	2[a]	500–580	553	550
Phenol red	4	2[a]	520–600	558	560

NOTE: For sulphonphthalein indicators such as bromocresol green and bromothymol blue and for phenolphthalein, the best choice of wavelength is the λ_{max} of the base form of the indicator because the base form has a higher absorbance at its λ_{max} than the acid form has at its λ_{max}. Also, the acid form generally absorbs very little at the λ_{max} of the base, whereas the base form absorbs significantly at the λ_{max} of the acid. The azo dyes methyl orange and methyl red have the opposite behavior, and the best wavelength for measuring their pK_a is the λ_{max} of the acid form.
[a]1 M NaOH; [b]1 M HCl.

at 590 nm was measured to determine the value of λ_{max} more precisely. Conditions for determining λ_{max} for all indicators are listed in Table 2.

The solution for determining the pK_a of bromophenol blue was prepared by dissolving 5.0 mL of 0.04% bromophenol blue solution and the contents of one pH 4 buffer capsule[1] in water in a 250-mL volumetric flask. Fifty milliliters of the solution was poured into each of five 100-mL beakers. Using a pH meter accurate to 0.01 pH unit, two of the solutions were adjusted to about pH 3.4 and pH 3.7 by dropwise addition of 1 M HCl. Two other solutions were adjusted to approximately pH 4.3 and pH 4.6 by dropwise addition of 1 M NaOH. The solution in the fifth beaker had a pH of about 4.0. The approximate pH values used for all the indicators are listed in Table 3. In each case, solutions were adjusted to pH values lower than that of the buffer capsule with 1 M HCl and to pH values higher than that of the buffer capsule with 1 M NaOH.

The absorbances of the five bromophenol blue solutions were measured with a Bausch & Lomb Spectronic 20D spectrophotometer. The pH 3.4 solution was then adjusted to about pH 2 with two drops of concentrated HCl solution to produce pure HIn, and the absorbance of the resulting solution was measured to determine A_{HIn}. Similarly, the pH 4.6 solution was adjusted to about pH 12 with two drops of 50% NaOH solution to produce pure In⁻, and the absorbance of the resulting solution was measured to determine A_{In^-}. The results for bromophenol blue are displayed in Table 4. The x-intercept from the plot of $\log_{10}[(A - A_{In^-})/(A_{HIn} - A)]$ vs pH (Fig. 1) was 3.95, and the slope was –0.96. The pK_a results for all the indicators investigated are listed in Table 5.

Discussion of Results

The average pK_a values for the majority of the indicators obtained using eq 3 have small standard deviations, and the slopes of the plots of eq 4 for the indicators are generally close to –1. However, the pK_a values of phenolphthalein determined by both methods show a much greater uncertainty. Phenolphthalein is a dibasic indicator, whose pK_a values are so similar that the spectrophotometric method does not produce accurate results (15). Methyl red is also a dibasic indicator with a small difference between pK_a values (16), but the standard deviation of the average pK_a value using eq 3 and the slope of the line from eq 4 have only slightly larger deviations than most of the other indicators. Other investigators have also found that methyl red produces reasonably accurate results (1, 7, 8).

The pK_a values determined by the algebraic method, using eq 3, and the graphical method, using eq 4, are essentially the same, even for phenolphthalein. Most of these values are within about 0.1 pH unit of the pK_a values found in the

Table 3. Solutions Used To Measure pK_a of Indicators

Indicator	Vol of Indicator/mL[a]	Buffer Capsule (pH)	Approximate pH Values
Bromocresol green	9.0	4	4.0, 4.3, 4.6, 4.9, 5.2
Bromocresol purple	7.0	7	5.4, 5.7, 6.0, 6.3, 6.6
Bromophenol blue	5.0	4	3.4, 3.7, 4.0, 4.3, 4.6
Bromothymol blue	9.0	7	6.4, 6.7, 7.0, 7.3, 7.6
Methyl orange	1.5	4	3.1, 3.4, 3.7, 4.0, 4.3
Methyl red[b]	1.5	4	4.4, 4.7, 5.0, 5.3, 5.6
Phenolphthalein	0.2	10[c]	8.8, 9.1, 9.4, 9.7, 10.0
Phenol red	3.0	7	7.2, 7.5, 7.8, 8.1, 8.4

[a]Volumes of indicator solutions were chosen such that the highest absorbance value for each indicator was between 0.7 and 1.0. Results were not as satisfactory when the highest absorbance value was significantly below or above this range.
[b]Some methyl red precipitated from solution. The solution was filtered before use.
[c]2.0 g of glycerin was added to prevent borax in the buffer from causing the color to fade.

Table 4. pK_a Determination for Bromophenol Blue

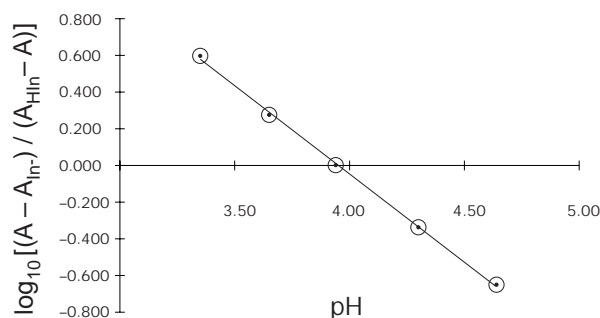| pH	Absorbance	$\log_{10}\left(\dfrac{A - A_{In^-}}{A_{HIn} - A}\right)$	pK_a from eq 3
3.35	0.170	0.60	3.95
3.65	0.287	0.28	3.93
3.94	0.411	0.00	3.94
4.30	0.562	-0.34	3.96
4.64	0.670	-0.65	3.99
		av	3.95 ± 0.02
12	A_{In^-} 0.818		
2	A_{HIn} 0.006		

Figure 1. Plot of $\log_{10}[(A - A_{In^-})/(A_{HIn} - A)]$ vs pH for bromophenol blue.

literature at the same ionic strength. The greatest difference was found for the pK_a of phenolphthalein, which was about 0.3–0.4 pH unit lower than the literature value.

This procedure uses fewer solutions than other published methods for finding the pK_a of an indicator. Solutions required prior to the lab can be prepared easily or purchased inexpensively. Students in the lab prepare just two solutions, the one used to determine the λ_{max} of the acid or base form of the indicator and the stock solution used to measure the pK_a of the indicator. The strong acids and bases used are somewhat dangerous to handle, but students would probably be familiar with their use from previous experiments. At the end of the experiment, the students themselves or technicians can neutralize the solutions generated during the experiment and pour them down the drain.

Conclusions

This procedure for the spectrophotometric determination of pK_a values of indicators is a good general chemistry lab experiment. It leads to accurate results using Spectronic 20's and pH meters found in most general chemistry labs. The lab procedure can conveniently be completed within three hours, because there are few solutions to prepare and other manipulations are kept to a minimum. In addition, students are probably familiar with the types of reagents used and could even dispose their own waste solutions at the end of the lab period.

Note

1. The contents of a pH 4 buffer capsule can be replaced by 1.0 g of potassium acid phthalate. A mixture of 0.37 g KH_2PO_4 and 0.60 g anhydrous Na_2HPO_4 can be substituted for the contents of a pH 7 buffer capsule.

Literature Cited

1. Brown, W. E.; Campbell, J. A. *J. Chem. Educ.* **1968,** *45,* 674–675. Several indicators were studied by the methods of Ramette (*4*) and Tobey (*7*).

2. Lai, S. T. F.; Burkhart, R. D. *J. Chem. Educ.* **1976,** *53,* 500. The authors assume that, for a number of indicators, the absorbances of HIn at the λ_{max} of In$^-$ and In$^-$ at the λ_{max} of HIn are negligible. Several solutions of an indicator are prepared with different pH values, and absorbances of the solutions at each λ_{max} are measured. The pK_a of the indicator is obtained from the equation pK = pH + log($-\Delta A_{In^-}A_{HIn}/\Delta A_{HIn}A_{In^-}$), where A_{HIn} is the absorbance of a solution at the λ_{max} of HIn, A_{In^-} is the absorbance of the solution at the λ_{max} of In$^-$, ΔA_{In^-} is the range of A_{In^-} values, and ΔA_{HIn} is the range of A_{HIn} values. (Note that this is the correct equation. The equation given in ref *2* is incorrect.) Data are presented for thymol blue.

3. Ramette, R. W. *Chemical Equilibrium and Analysis*; Addison-Wesley: Reading, MA, 1981; pp 676–681. In a general procedure, students measure the absorption spectra of two solutions containing the acidic and basic forms of an indicator to determine its analytical wavelength, λ_{max}, or the instructor tells them λ_{max}. The absorbances of the acid and base forms of the indicator at λ_{max}, A_{HIn} and A_{In^-}, respectively, are used in eq 2 to calculate [HIn]/[In$^-$]. Three solutions of the indicator with different pH's around its pK_a value are prepared by students using an acid–conjugate base buffer, where the pK_a of the acid is near the pK_a of the indicator. They measure the absorbances and calculate the ionic strengths of these solutions. Everyone determines the pK_a value for each buffered solution using concentration and absorbance data and activity coefficients, then averages the values.

4. Ramette, R. W. *J. Chem. Educ.* **1963,** *40,* 252–254. Each student is assigned a different ionic strength at which to prepare solutions of bromcresol green at different pH's to determine the concentration quotient, *Q*, of the indicator. First, he or she prepares a solution of the indicator in sodium acetate solution, using KCl to achieve the ionic strength, and measures the absorption spectrum of the solution. The student then adds several aliquots of acetic acid solution and finally an aliquot of hydrochloric acid solution to the indicator solution. After each aliquot is added, the absorbance

Table 5. Results of Measurement of pK_a Values of Indicators

Indicator	Lit Value (*13*) of pK_a at Ionic Strength			Ionic Strength Range Used	pK_a from Eq 3	pK_a from Eq 4	Slope of Eq 4 Plot
	0.01	0.05	0.10				
Bromocresol green	4.80	4.70	4.66	0.02–0.04	4.62 ± 0.02	4.62	−1.04
Bromocresol purple	6.28	6.21	6.12	0.02–0.05	6.18 ± 0.03	6.19	−0.94
Bromophenol blue	4.06	4.00	3.85	0.02–0.03	3.95 ± 0.02	3.95	−0.96
Bromothymol blue	7.19	7.13	7.10	0.04–0.08	7.00 ± 0.02	7.00	−1.00
Methyl orange	3.46	3.46	3.46	0.02	3.42 ± 0.02	3.43	−1.04
Methyl red	5.00	5.00	5.00	0.03–0.06	4.91 ± 0.05	4.90	−0.91
Phenolphthalein	–	–	9.7[a]	~0.1	9.34 ± 0.20	9.37	−1.36
Phenol red	7.92	7.84	7.81	0.07–0.09	7.65 ± 0.02	7.66	−1.03

NOTE: The volumes of acid and base solutions added to the buffered indicator solutions were small compared to that of the indicator solution itself. Calculations do not need to take this dilution into account, because it does not affect the values of the pK_a.
[a]Reference *14*.

of the resulting solution is measured at λ_{max}, except that the entire spectra of the solutions containing 1:1 acetate:acetic acid and hydrochloric acid are recorded. Absorption readings are corrected for dilution. Each student calculates the hydrogen ion concentration of each solution using the dissociation quotient of acetic acid at his or her assigned ionic strength. They calculate pQ values for each solution using eq 3, then determine an average value. The class pools their average pQ values at different ionic strengths, then each person plots pQ vs log f, using the equation $pQ = pK_a + \log f$. In the equation, f is the ratio of activity coefficients and K_a is the acid dissociation constant for the indicator using activities. The y-intercept of the graph is pK_a.

5. Salzberg, H. W.; Morrow, J. I.; Cohen, S. R.; Green, M. E. *Physical Chemistry Laboratory: Principles and Experiments*; Macmillan: New York, 1978; pp 402–405. Students measure the absorption spectra of two solutions containing the acidic and basic forms of bromophenol blue to determine its analytical wavelength, λ_{max}. Next, they dilute solutions containing the indicator until one of the solutions has an absorbance of 0.9–1.0 at λ_{max}. They further dilute this solution to 0.2, 0.4, 0.6, and 0.8 times its original strength. They measure the absorbance of the diluted solutions at λ_{max} and prepare a Beer's law plot from the absorbances of the five solutions. Each person prepares several solutions with pHs between 3.4 and 4.6 that have the same total concentration of bromophenol blue as the solution with an absorbance of 0.9–1.0. The solutions are prepared in buffers in this pH range, or the pH is adjusted with hydrochloric acid or ammonia solution. Students measure the absorbance of these solutions at λ_{max}. They obtain the pK_a of bromophenol blue from eq 1 using absorbancies from the Beer's law data and the absorbances of the pH 3.4–4.6 solutions or from a plot of eq 3, similar to the method described here.

6. Sawyer, D. T.; Heineman, W. R.; Beebe, J. M. *Chemistry Experiments for Instrumental Methods*; Wiley: New York, 1984; pp 193–198. Students measure the absorption spectra of solutions of bromothymol blue at pH 1, 7, and 13 and choose two wavelengths to the left and right of the isosbestic point that have maximum differences between the absorbances of the acid and base forms of the indicator. They prepare solutions of the indicator at seven other pH values using phosphate buffers and measure the absorbances of the solutions at the two wavelengths. For each wavelength, students plot A vs pH using the data from the nine solutions. The pK_a is equal to the pH at the inflection point of each curve. Also, they determine the ratios of $[In^{2-}]/[[HIn^-]$ for each solution from one of the curves and plot $\log_{10}[In^{2-}]/[[HIn^-]$ vs pH, using an equation derived from eq 1. The pK_a is the y-intercept of the graph.

7. Tobey, S. W. *J. Chem. Educ.* **1958,** *35*, 514–515. The absorption spectra of the acidic and basic forms of methyl red were measured to determine their respective λ_{max} values. The absorbancies of both the acidic and basic forms at both λ_{max} values were determined using Beer's law plots. Four solutions of methyl red with the same ionic strength but different pH's were prepared using the same concentration of sodium acetate and different concentrations of acetic acid. The pH of each solution was measured with a pH meter, and the absorbance was measured at the λ_{max} value of both the acidic and basic forms. Hydrogen ion concentrations from pH values and concentrations of the acidic and basic forms of methyl red in the four solutions from the absorbance and absorbancy data were used to calculate pK_a values for each solution. The values were averaged.

8. Walters, D.; Birk, J. P. *J. Chem. Educ.* **1990,** *67*, A252–A258. Methyl orange, methyl red, and phenolphthalein were studied. A number of solutions of each indicator were prepared using buffers that produced a range of pH values such that the solution with lowest pH contained the pure acid form of the indicator and the solution with highest pH contained the pure base form. The absorbance of each solution was measured, and plots of $(A_{HIn} - A_{In^-})/(A - A_{HIn})$ vs $[H^+]^{-1}$ from the equation $(A_{HIn} - A_{In^-})/(A - A_{HIn}) = 1 + K_a[H^+]^{-1}$ produced straight lines with slopes equal to K_a. This equation can be derived from eq 3.

9. Willard, H. H.; Merritt, Jr., L. L.; Dean, J. A. *Instrumental Methods of Analysis*, 4th ed; Van Nostrand: New York, 1965; pp 108–109. Students obtain the experimental data for bromcresol green by the method of Ramette (*4*), except that they measure pH with a pH meter and everyone uses the same ionic strength. They determine values for pK_a by both methods described by Sawyer et al. (*6*).

10. Ramette, R. W. *Chemical Equilibrium and Analysis*; Addison-Wesley: Reading, MA, 1981; Chapter 13.

11. Ramette, R. W. *J. Chem. Educ.* **1967,** *44*, 647–654.

12. *Lange's Handbook of Chemistry*, Dean, J. A., Ed.; McGraw-Hill: New York, 1992; pp 8.115–8.116.

13. *Handbook of Analytical Chemistry*, Meites, L., Ed.; McGraw-Hill: New York, 1963; Sec. 3 p 36.

14. Skoog, D. A.; West, D. M. *Analytical Chemistry: An Introduction*, 4th ed.; Saunders: Philadelphia, 1986; p 164.

15. Kolthoff, I. M. *Acid–Base Indicators*, Rosenblum, C., Translator; Macmillan: New York, 1937; pp 112 and 221–224.

16. Ramette, R. W.; Dratz, E. A.; Kelly, P. W. *J. Phys. Chem.* **1962,** *66*, 527–532.