A Colorful Investigation of a Diprotic Acid: A General Chemistry Laboratory Exercise

Eugene T. Smith and John R. Matachek

Department of Chemistry, Hamline University, St. Paul, MN 55104, gsmith@gw.hamline.edu

Received April 26, 2002. Accepted August 5, 2002.

Abstract: A general chemistry laboratory experiment that can be completed in a single laboratory period is described that familiarizes students with the acid–base chemistry of a diprotic acid and with the use of visible spectroscopy to determine species concentrations. This experiment is a modified version of a previously described laboratory exercise developed for an upper-division quantitative analysis course. Students work in teams and as a class to generate different ionization states of various highly absorbing dyes. Both spectroscopic and potentiometric (pH) data is collected using LabWorks II stations, but other inexpensive pH meters and visible spectrometers (e.g., Spec 20s) are suitable. A spreadsheet template is used to determine the percent composition of various ionization states of a diprotic acid and to determine the pK_a values. Besides introducing students to fundamental tools and key chemical concepts, this laboratory is also inexpensive to operate and utilizes nontoxic, colorful solutions.

Introduction

A creative upper-level undergraduate experiment that entailed the analysis of a diprotic dye, thymol blue, was recently described in this journal [1]. The experiment is visually interesting as the neutral acid and each of its ionization states are uniquely colored. The authors introduced students to many fundamental topics, including titrations and calibration curves, the spectroscopic determination of extinction coefficients, the determination of component concentrations in mixtures, fractional concentrations (α values), and acid dissociation constants (pK_a values). Students worked in groups over a number of laboratory periods in this rather comprehensive spectroscopic and potentiometric analysis of thymol blue.

Such fundamental topics as concentrations in mixtures and pK_a values of polyprotic acids are usually covered in general chemistry courses; thus, we have significantly simplified and modified this previously described advanced-level experiment so that it is suitable for a general chemistry laboratory experiment. Students work in teams to prepare and spectroscopically analyze solutions at various pH values, and then they compile their results with the rest of the class. In this manner, the experiment can be completed in a single laboratory period. Another diprotic dye, cresol red was analyzed, and students were asked to identify their unknown acid based on their experimentally determined pK_a values.

All of the data is collected using a LabWorks II interface, associated probes, and a laptop computer. The pH data and percent transmittance data are collected via the LabWorks II station, and the data are manually entered by the students onto an Excel worksheet. The data collected by each group is compiled with those of their classmates for each dye, and a spreadsheet template is used to automatically calculate percent composition of each ionization state. In order to determine percent composition, a spreadsheet is employed to solve a 3 × 3 matrix. This step is only briefly discussed in the laboratory because it is beyond the scope of a typical introductory general chemistry class.

Advantages of this experiment include that it is inexpensive to run with existing equipment, the equipment is typically available to general chemistry students, it familiarizes students with spreadsheets, and it is fun.

Experimental

Chemicals. Sufficient volumes of the acidic, basic, and neutral form of both cresol red (0.005 g L^{-1}) and thymol blue (0.005 g L^{-1}) were prepared by first dissolving the appropriate amount of the dye in distilled water. Each dye solution was then split into three separate portions. The acidic and basic forms were made by adding about 20 mL L^{-1} of either 12 M HCl or 18 M NaOH. The preparation of these solutions can be performed in front of the students so they realize that they are still working with the same solution, the different colors that are observed are due to different ionization states of the acids.

Once the acidic and basic forms of the unknown are prepared, students combine the different solutions to obtain samples at the appropriate pH values that are needed for the experiment. This process cuts down on the handling of concentrated acids and bases by the students, and it minimizes potential dilution errors.

Instrumentation. Laptop-controlled LabWorks II stations were fitted with combination pH electrodes and spectroscopic cell holders. Inexpensive LEDs were used as spectrometer sources. LEDs emitting at 430, 565, and 600 nm are available with LabWorks II stations; however, these LEDs did not suffice as adequate sources when used in conjunction with narrow bandpass interference filters (see below). High intensity LEDs emitting at appropriate wavelengths were purchased from Radio Shack and installed into the LED jacks used by the LabWorks II spectrometers. The emission spectra of the LEDs supplied with LabWorks II stations collected with an Ocean Optics diode-array spectrometer are shown in Figure 1.

The LEDs were chosen to correspond as closely as possible to λ_{max} for the different ionization states of the dyes. The absorption spectra of various ionization states of the dyes were collected using a diode-array spectrometer (HP8452), and the spectra of cresol red and thymol blue are shown in Figures 2 and 3, respectively. The broad bandwidth of the LEDs were a problem because their emission spectra overlapped not only with λ_{max} for the ionization state of interest, but

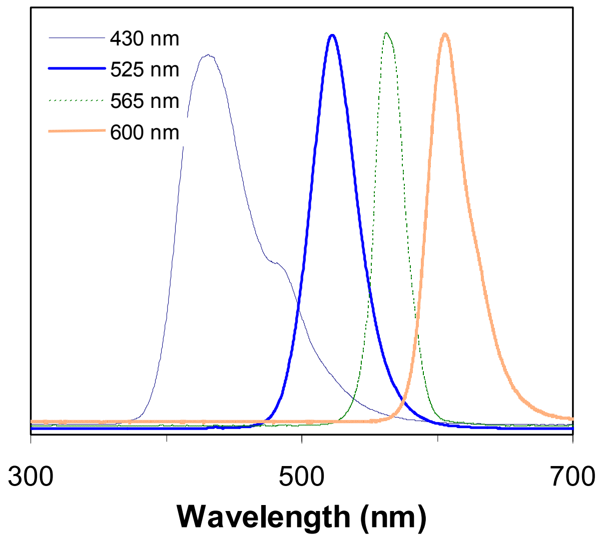


Figure 1. Emission spectra of LEDs from LabWorks II stations.

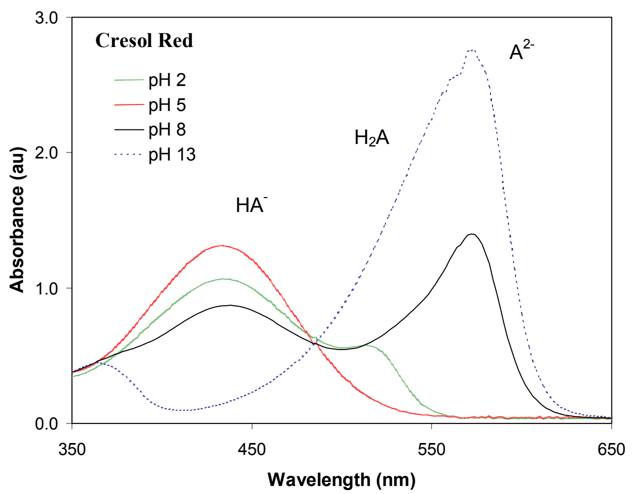


Figure 2. Absorption spectra of approximately 5 ppm cresol red at various pH values

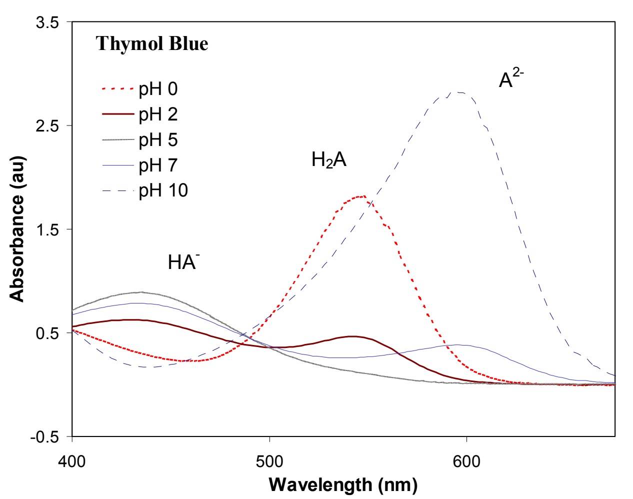


Figure 3. Absorption spectra of approximately 5 ppm thymol blue at various pH values.

also with the shoulders of the absorbance spectra of other ionization states. Because Beer's law only applies to monochromatic light, the relationship between absorbance and concentration is not accurate. This problem with the source, which is illustrated in Figure 4, was resolved through the use of an 11.8-mm diameter narrow-bandpass interference filter (Edmund Scientific). The filter reduces the bandwidth to 2 nm and the intensity of the source approximately 10 fold (emission spectra of the source is not shown in Figure 4).

A simple spectrometer similar to the LabWorks II spectrometer, but modified to hold the optical filters, was constructed out of wood. A separate spectrometer was set up for each wavelength, and students moved from spectrometer to spectrometer in order to obtain their percent transmittance data at three separate wavelengths.

An alternative approach to obtaining spectroscopic data is to use Spec 20s or other scanning or diode-array spectrometers, and other pH meters can be used instead of the LabWorks II stations.

Equipment and Supplies. The equipment needed for each group is listed in Table 1.

Data Collection. The class is divided into teams of 3 to 4 students. Each team is instructed to adjust the pH of the stock solution in incremental units as specified in their laboratory handout such that the four teams will have solutions for the same dye from pH 0 to 13. Obtaining a solution at pH 14 is difficult without significant dilution. The teams then read the percent transmittance of their solutions at three separate wavelengths, and they compile this information with the results of the entire class.

Results

Data Analysis. The relative percent composition of each ionization state present and a plot of percent composition versus pH are automatically generated by the spreadsheet after the teams have entered all their percent transmittance data. Typical data for cresol red and thymol blue are shown in Figures 5 and 6, respectively. Deviations between experimental data (symbols) and theoretical expectations (solid lines), as illustrated in Figure 6, typically occur when solutions are not thoroughly stirred.

Calculation of percent composition. The determination of percent composition of each ionization state as a function of pH involves a number of steps. The first step involves the conversion of percent transmittance for three separate wavelengths at each pH increment to absorbances. The total absorbance at each wavelength is as follows:

$$A_{x,\mathrm{total}} = \varepsilon_{x,\mathrm{H_2A}} b C_{\mathrm{H_2A}} + \varepsilon_{x,\mathrm{HA^-}} + \varepsilon_{x,A^{2-}} b C_{\mathrm{A^{2-}}}$$

The extinction coefficients (ε) for cresol red and thymol blue are listed in Table 2. The values for cresol red were determined by serial dilutions as previously described [1] and those of thymol blue were extracted from the literature [1].

Next, a 3 × 3 matrix is solved to determine the concentrations of each species at a given pH (see Figure 7 and 8 for documentation). Only a brief mention of this step is provided to the students as this is beyond the scope of an introductory general chemistry class. Once the concentrations are determined, the percent composition is easily found, that is,

$$\%\ \mathrm{H_2A} = ([\mathrm{H_2A}]/([\mathrm{H_2A}] + [\mathrm{HA^-}] + [\mathrm{A^{2-}}])) \times 100\ \%$$

All of these calculations can be done in a single step on a spreadsheet.

Simulation of percent composition. The percent composition of H_2A, HA^-, and A_2^- as a function of pH are

© 2002 Springer-Verlag New York, Inc., S1430-4171(02)06619-6, Published on Web 11/1/2002, 10.1007/s00897020619a, 760359es.pdf

Table 1. Student Supplies

5 mL vials w/caps (4)
100 mL beaker (3)
stir bar and stir plate
pasteur pipets
pipet bulbs (3–4)
disposable plastic cuvets (5)
Wash bottle

Table 2. Extinction Coefficients (Thymol Blue Taken From Ref 1)

	H_2A	HA^-	A^{2-}
Cresol Red			
440 nm	3065	24137	2490
518 nm	40230	2682	23946
574 nm	577	96	49808
Thymol Blue			
436 nm	6780	16700	2870
545 nm	41100	1560	21500
595 nm	6440	404	40000

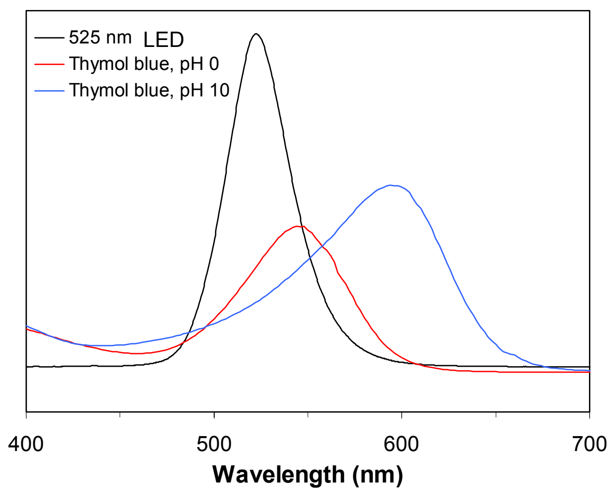


Figure 4. Emission spectra of a 525-nm LED and absorption spectra of approximately 5 ppm thymol blue at pH 0 and pH 10. The broad bandwidth of the LED overlaps a significant portion of both absorption spectra and therefore does not give accurate information about species concentration.

determined from the following expressions [2], respectively (× 100%):

$$[H_2A]/C_A = \frac{[H^+]^2}{[H^+]^2 + K_{a_1}[H^+] + K_{a_1}K_{a_2}}$$

$$[HA^-]/C_A = \frac{K_{a_1}[H^+]}{[H^+]^2 + K_{a_1} + K_{a_1}K_{a_2}}$$

$$[A^{2-}]/C_A = \frac{K_{a_1}K_{a_2}}{[H^+]^2 + K_{a_1}[H^+] + K_{a_1}K_{a_2}}$$

where C_A is the total concentration of the diprotic acid, including all ionization states. The documentation for simulating the expected percent composition of the diprotic acid as a function of pH is shown in Figures 7 and 8. The calculated curves in the student=s spreadsheet is based on their estimated K_a values.

Determination of pK_a Values. Each group of students is asked to estimate from the graph of their experimental data the value of pK_{a1} (where the percent compositions of H_2A and HA^- are 50 %) and pK_{a2} (where the % composition of HA^- and A^{2-} are 50%). These two pK_a values are entered in the appropriate space on their spreadsheet (first line of the quality of fit table). The quality of fit or residuals is calculated as follows:

$$\text{Quality of fit} = (\Sigma\ (\%\ \text{composition}_{calc} - \%\ \text{composition}_{exp})^2)^2$$

and documentation for determining this value is shown in Figures 7 and 8. After inputting their initial estimate of the pK_a, they adjust the value of one of their pK_a values in ± 0.1 increments. The calculated quality of fit appears on one line of the spreadsheet. They keep adjusting the pK_a until they obtain a minimal value in the difference between their experimental results and the simulation. This is repeated for the second pK_a value while holding the other pK_a value constant. In order to keep track of the best fit, they copy/paste special (value) the quality of fit results for each estimated pK_a value into a table (see spreadsheet for examples of estimations that were made, and the quality of fit). Once this minimization has been completed, they identify their unknown from a table of pK_a values for the various diprotic acids.

Because this is a class experiment, we do not have sufficient data at this time to determine a standard deviation for the pK_a values. We have observed that the pK_a values were determined accurately within ±0.2 pK_a units when a diode-array spectrometer was used, and larger deviations were observed with our homemade spectrometers (±0.5 pK_a units). It is very important that students take care to completely mix their solutions in order to obtain good results.

Discussion

A previously published laboratory exercise [1] describes the extensive potentiometric and spectroscopic analysis of thymol blue for applications in an upper-division quantitative analysis course. In this application, we describe a simplified version of this experiment and the modifications make it appropriate for use in a general chemistry course. It can be done in a single laboratory period, including the calculations, which are completed using a spreadsheet template. Student data appear on the first page of the spreadsheet template (Figures 5 and 6). The second page of the spreadsheet is used to do all the calculations (Figures 7 and 8). It is not necessary to go over the second page of the template with the students because it is beyond the scope of the course. The correct template for each acid must be supplied to the various teams because the second page of the template contains the correct extinction coefficients for their dye.

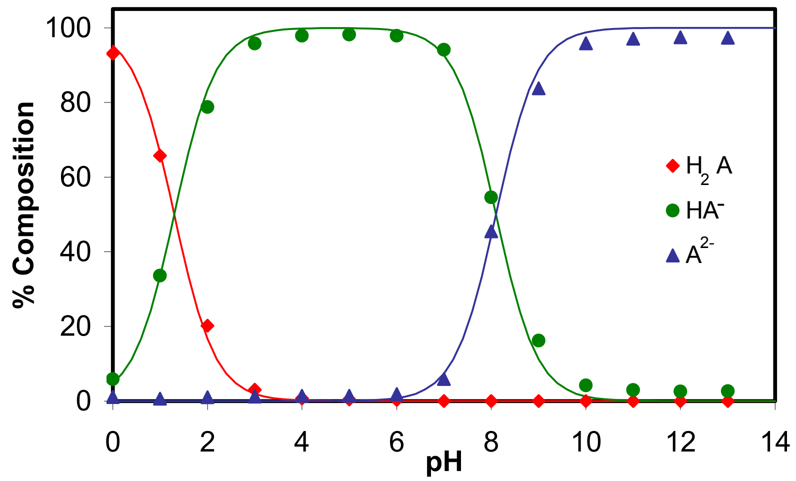
Students learn about determining the concentrations and pK_a values of polyprotic acids through this inexpensive, very colorful experiment. This experiment has students work in groups using fundamental scientific equipment and spreadsheets. Our students have enjoyed performing this experiment.

 S1430-4171(02)06619-6, Published on Web 11/1/2002, 10.1007/s00897020619a, 760359es.pdf

Names: **Cresol Red**

λ (nm)	pH 0	pH 1	pH 2	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10	pH 11	pH 12	pH 13	pH 14
440	57.7	21.3	8.8	6.9	5.1	5.1	5.4	5.6	13.5	44.1	64.5	66.9	67.6	67.3	
518	0.8	1.5	27.3	62.6	66.4	67.4	67.5	62.3	24.4	7.6	5.3	5.2	5.1	5.0	
574	86.9	89.3	91.5	92.0	90.2	90.3	88.3	68.3	4.0	0.3	0.2	0.2	0.2	0.2	

Percent Composition															
H_2A	93	66	20	3	1	0	0	0	0	0	0	0	0	0	0
HA^-	6	34	79	96	98	98	98	94	55	16	4	3	3	3	0
A^{2-}	1	1	1	1	1	1	2	6	45	84	96	97	97	97	100



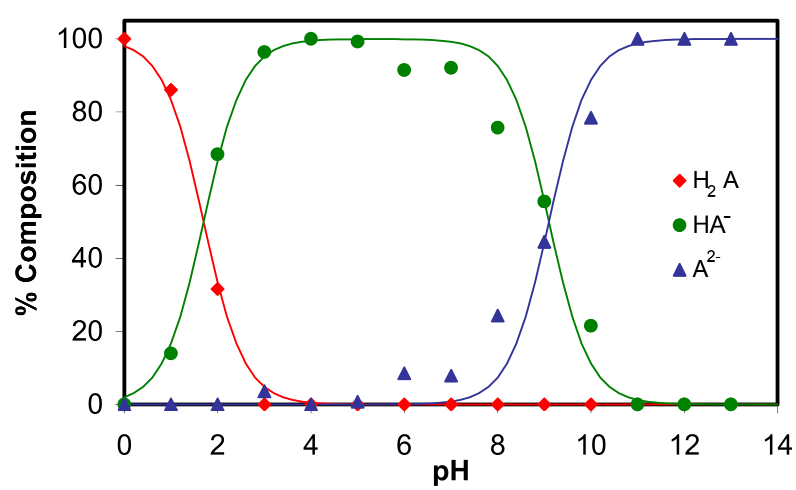
pK_{a1}	pK_{a2}	Quality of fit H_2A	HA^-	A^{2-}
1.3	8.1	4.5	9.8	8.2
1.0	8.0	19.5	23.6	11.1
1.1	8.0	13.6	18.7	11.1
1.2	8.0	8.1	14.6	11.1
1.3	8.0	4.5	12.2	11.1
1.4	8.0	6.7	12.5	11.1
1.3	8.0	4.5	12.2	11.1
1.3	8.1	4.5	9.8	8.2
1.3	8.2	4.5	10.8	9.5
1.3	8.3	4.5	14.5	13.5
1.3	8.4	4.5	19.2	18.5
1.3	8.5	4.5	24.2	23.7

Figure 5. Typical data sheet for cresol red that includes percent transmittance and concentration data, plot of concentration data and trace of calculated concentrations based on acid dissociation constants, and a table of estimated acid dissociation constants.

Names: **Thymol Blue**

λ (nm)	pH 0	pH 1	pH 2	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10	pH 11	pH 12	pH 13	pH 14
436	67.8	56.8	29.4	20.6	20.8	21.3	24.8	26.1	35.6	44.3	62.8	85.9	88.7	88.4	93.8
545	5.4	8.5	28.6	83.8	94.8	86.3	75.9	77.8	63.4	46.1	26.1	15.3	16.7	16.7	24.7
595	67.1	69.2	84.1	84.1	105.9	94.0	71.4	74.0	46.1	24.7	7.9	2.8	3.2	3.2	6.3

Percent Composition															
H_2A	100	86	32	0	0	0	0	0	0	0	0	0	0	0	0
HA^-	0	14	68	96	100	99	92	92	76	56	22	0	0	0	0
A^{2-}	0	0	0	4	0	1	8	8	24	44	78	100	100	100	100



pK_{a1}	pK_{a2}	Quality of fit H_2A	HA^-	A^{2-}
1.7	9.1	6.1	23.1	23.0
1.5	9.0	13.3	26.5	23.4
1.6	9.0	8.2	24.3	23.4
1.7	9.0	6.1	23.5	23.4
1.8	9.0	9.4	24.4	23.4
1.9	9.0	15.0	26.8	23.4
1.7	8.8	6.1	27.6	27.6
1.7	8.9	6.1	25.1	25.0
1.7	9.0	6.1	23.5	23.4
1.7	9.1	6.1	23.1	23.0
1.7	9.2	6.1	24.0	23.9
1.7	9.3	6.1	26.0	25.9

Figure 6. Typical data sheet for thymol blue that includes percent transmittance and concentration data, plot of concentration data and trace of calculated concentrations based on acid dissociation constants, and a table of estimated acid dissociation constants.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1	λ (nm)	ε_0	ε_6	ε_{13}		pK_1	1.3	4.45					Cresol Red			
2	440	3065	24137	2490		pK_2	8.1	9.76								
3	518	40230	2682	23946				8.25								
4	574	577	96	49808												
5																
6	pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
7	$[H_2A]$	5.18E-05	4.34E-05	1.08E-05	1.50E-06	3.93E							00	0.00E+00	0.00E+00	#NUM!
8	$[HA^-]$	3.26E-06	2.22E-05	4.23E-05	4.79E-05	5.35E							06	1.44E-06	1.51E-06	#NUM!
9	$[A^{2-}]$	6.19E-07	4.45E-07	5.68E-07	6.20E-07	7.91E							05	5.52E-05	5.53E-05	#NUM!

	A	B	C	D
10				
11				
12	pH	α1	α2	α3
13	0.0	95.2	4.8	0.0
14	0.2	92.6	7.4	0.0
15	0.4	88.8	11.2	0.0
16	0.6	83.4	16.6	0.0
17	0.8	76.0	24.0	0.0
18	1.0	66.6	33.4	0.0
19	1.2	55.7	44.3	0.0
20	1.4	44.3	55.7	0.0
21	1.6	33.4	66.6	0.0
22	1.8	24.0	76.0	0.0
23	2.0	16.6	83.4	0.0
24	2.2	11.2	88.8	0.0
25	2.4	7.4	92.6	0.0
26	2.6	4.8	95.2	0.0
27	2.8	3.1	96.9	0.0
28	3.0	2.0	98.0	0.0
29	3.2	1.2	98.8	0.0
30	3.4	0.8	99.2	0.0
31	3.6	0.5	99.5	0.0
32	3.8	0.3	99.7	0.0
33	4.0	0.2	99.8	0.0
34	4.2	0.1	99.9	0.0
35	4.4	0.1	99.9	0.0
36	4.6	0.1	99.9	0.0
37	4.8	0.0	99.9	0.1
38	5.0	0.0	99.9	0.1
39	5.2	0.0	99.9	0.1
40	5.4	0.0	99.8	0.2
41	5.6	0.0	99.7	0.3
42	5.8	0.0	99.5	0.5
43	6.0	0.0	99.2	0.8
44	6.2	0.0	98.8	1.2
45	6.4	0.0	98.0	2.0

Documentation for obtaining pK_a minmum

=SQRT(($B$13-sheet1!B9)^2+($B$18-sheet1!C9)^2 + ($B$23 -sheet1!D9)^2 + ($B$28-sheet1!E9)^2 + ($B$33-sheet1!F9)^2 + ($B$38-sheet1!G9)^2 + ($B$43 -sheet1!H9)^2 + ($B$48 -sheet1!I9)^2 +($B$53 -sheet1!J9)^2 + ($B$58 -sheet1!K9)^2 + ($B$63 -sheet1!L9)^2 + ($B$68 -sheet1!M9)^2 + ($B$73 -sheet1!N9)^2 + ($B$78 -sheet1!O9)^2 + ($B$83 -sheet1!P9)^2)

Documentation for solving 3x3 matrix and determination of % composition

=IF(MMULT(MINVERSE(sheet2!$B$2:$D$4),-1*LOG(sheet1!B4:B6*0.01))<0,0,MMULT(MINVERSE(sheet2!$B$2:$D$4),-1*LOG(sheet1!B4:B6*0.01)))

Documentation for simulating % composition

=((10^(-A13))^2)/(((10^(-A13))^2) +(10^(-A13)*10^(-$G$1)) + (10^(-$G$1) *10^(-$G$2)))*100

=(10^(-A13)*10^(-$G$1))/(((10^(-A13))^2) +(10^(-A13)*10^(-$G$1)) + (10^(-$G$1) *10^(-$G$2)))*100

=(10^(-$G$1) *10^(-$G$2))/(((10^(-A13))^2) +(10^(-A13)*10^(-$G$1)) + (10^(-$G$1) *10^(-$G$2)))*100

Figure 7. Documentation for the calculations and pK_a simulations of cresol red.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1	λ (nm)	ε_0	ε_6	ε_{13}		pK_1	1.7	6.10					Thymol Blue			
2	436	6780	16700	2870		pk_2	9.1	23.08								
3	545	41100	1560	21500				23.02								
4	595	6440	404	40000												
5																
6	pH	0	1	2	3	4								12	13	14
7	$[H_2A]$	3.14E-05	2.60E-05	1.24E-05	0.00E+00	0.00							0	0.00E+00	0.00E+00	0.00E+00
8	$[HA^-]$	0.00E+00	4.22E-06	2.68E-05	4.11E-05	4.12							0	0.00E+00	0.00E+00	0.00E+00
9	$[A^{2-}]$	0.00E+00	0.00E+00	0.00E+00	1.54E-06	0.00							5	3.74E-05	3.74E-05	3.03E-05

	A	B	C	D
10				
11				
12	pH	α1	α2	α3
13	0.0	98.0	2.0	0.0
14	0.2	96.9	3.1	0.0
15	0.4	95.2	4.8	0.0
16	0.6	92.6	7.4	0.0
17	0.8	88.8	11.2	0.0
18	1.0	83.4	16.6	0.0
19	1.2	76.0	24.0	0.0
20	1.4	66.6	33.4	0.0
21	1.6	55.7	44.3	0.0
22	1.8	44.3	55.7	0.0
23	2.0	33.4	66.6	0.0
24	2.2	24.0	76.0	0.0
25	2.4	16.6	83.4	0.0
26	2.6	11.2	88.8	0.0
27	2.8	7.4	92.6	0.0
28	3.0	4.8	95.2	0.0
29	3.2	3.1	96.9	0.0
30	3.4	2.0	98.0	0.0
31	3.6	1.2	98.8	0.0
32	3.8	0.8	99.2	0.0
33	4.0	0.5	99.5	0.0
34	4.2	0.3	99.7	0.0
35	4.4	0.2	99.8	0.0
36	4.6	0.1	99.9	0.0
37	4.8	0.1	99.9	0.0
38	5.0	0.1	99.9	0.0
39	5.2	0.0	100.0	0.0
40	5.4	0.0	100.0	0.0
41	5.6	0.0	100.0	0.0
42	5.8	0.0	99.9	0.1

Documentation for obtaining pK_a minimum

=SQRT(($B$13-sheet1!B9)^2+($B$18-sheet1!C9)^2 + ($B$23 -sheet1!D9)^2 + ($B$28-sheet1!E9)^2 + ($B$33-sheet1!F9)^2 + ($B$38-sheet1!G9)^2 + ($B$43 -sheet1!H9)^2 + ($B$48 -sheet1!I9)^2 +($B$53 -sheet1!J9)^2 + ($B$58 -sheet1!K9)^2 + ($B$63 -sheet1!L9)^2 + ($B$68 -sheet1!M9)^2 + ($B$73 -sheet1!N9)^2 + ($B$78 -sheet1!O9)^2 + ($B$83 -sheet1!P9)^2)

Documentation for solving 3 x 3 matrix and determination of % composition

=IF(MMULT(MINVERSE(sheet2!$B$2:$D$4),-1*LOG(sheet1!B4:B6*0.01))<0, 0,MMULT(MINVERSE(sheet2!$B$2:$D$4),-1*LOG(sheet1!B4:B6*0.01)))

Documentation for simulating % composition

=((10^(-A13))^2)/(((10^(-A13))^2) +(10^(-A13)*10^(-$G$1)) + (10^(-$G$1) *10^(-$G$2)))*100

=(10^(-A13)*10^(-$G$1))/(((10^(-A13))^2) +(10^(-A13)*10^(-$G$1)) + (10^(-$G$1) *10^(-$G$2)))*100

=(10^(-$G$1) *10^(-$G$2))/(((10^(-A13))^2) +(10^(-A13)*10^(-$G$1)) + (10^(-$G$1) *10^(-$G$2)))*100

Figure 8. Documentation for the calculations and pK_a simulations of thymol blue.

Acknowledgment. This work was supported by grants from the Fairchild Foundation and the National Science Foundation (GOALI award CHE-9901782).

Supporting Materials. A laboratory handout for students and the Excel worksheets that produced Figures 5–8 are available in a Zip file (http://dx.doi.org/10.1007/s00897000619b)

References and Notes

1. Russell, D. D.; Potts, J.; Russell, R. M.; Olson, C.; Schimpf, M. *Chem. Educator* [Online] **1999,** *4* (2), 68–72; S1430-4171(99)02288-6; DOI 10.1007/s00897990288a
2. Skoog, D. A.; West, D. M; Holler, F. J; Crouch, S. R. *Analytical Chemistry,* 7th ed. Saunders Publishing: Orlando, FL, 2000.