

Experiment # 11: Spectroscopic determination of indicator pKa

pH indicators may be defined as highly colored Bronsted-Lowry acid-base conjugate. In many indicator systems and, within the pH transition range, the observed color is really a mixture of the two forms.

The ratio of concentrations of the conjugate acid and base forms in a buffer solution, as indicated by the same equation as that used for determining the pKa, is given by the Henderson-Hasselbalch equation:

$$\log \frac{[\text{conjugate base}]}{[\text{conjugate acid}]} = \log \frac{[\text{Ind}^-]}{[\text{HInd}]} = \text{pH} - \text{pK}_a$$

where HInd and Ind⁻ represent the acidic and anionic (or basic) forms of the indicator, respectively.

The indicator concentration ratio is controlled by the pH of the solution, whereas the buffer concentration ratio controls the solution pH. At first glance, this statement seems contradictory. In reality, however, it is simply a matter of relative concentrations. The buffer components are present in high concentrations, so they control the pH of the buffer solution via the conventional acid-base reactions. On the other hand, the indicator species are present in low, even negligible, amounts relative to the other acid-base systems in the solution. In terms of visible absorption, however, the indicator species predominate over the buffer components (most of which are colorless).

Procedures for determining solution pH using a short range of visual comparisons of indicator colors can usually distinguish 0.2 pH unit differences.

Table I

Table II

sample #	mL Hind	mL salt	mL acid	salt/acid ratio	log ratio	buffer pH
1	2.00	0.00	8.00	-----	-----	----
2	2.00	2.00	6.00			
3	2.00	4.00	4.00			
4	2.00	6.00	2.00			
5	2.00	8.00	0.00	-----	-----	

Calculate the pH of each buffer mixture using the original Henderson-Hasselbalch equation: $\text{pH} = \text{pK}_a + \log ([\text{salt}] / [\text{acid}])$. The pK_a in this equation is for the dissociation of acetic acid as determined in a previous experiment (it should have a value of about 4.62). Notice that the dilution effect from adding the indicator cancels in the buffer salt/acid ratio.

Measurement of indicator/buffer absorbances

Turn on a Spectronic 20, and allow the instrument to warm-up. Set the wavelength dial to λ_{max} for the base form of the indicator chosen for study. Place each of the indicator/buffer solutions in a clean, dry, or properly rinsed cuvette. Use deionized water in a sixth cuvette to calibrate the spectrometer to read 100% T.

Record the observed %T (to $\pm 0.1\%$) and A for each of the samples in data Table III, and calculate A_{calc} using the equation: $A = 2 - \log \%T$

Table III

Sample #	% T.	A_{meas}	A_{calc}
1			$= A_a$
2			

Determination of indicator pK_a

Use the absorbance values recorded in Table III to calculate the indicator pK_a's for the buffer mixtures (Samples #2, #3, and #4). Complete the entry columns in Table IV, and calculate the indicator pK_a for the modified Henderson-Hasselbalch equation:

$$\text{pK}_a = \text{pH} - \log \frac{[A_i - A_a]}{[A_b - A_i]}$$

Table IV

Sample #	(A _i -A _a)	(A _b -A _i)	$\frac{[A_i - A_a]}{[A_b - A_i]}$	Log ratio	Hind pK _a
2					
3					
4					

Data treatment and report

A two-page report is required for this experiment. On the first page, under appropriate headings, make complete copies of Tables II, III, and IV. List the name (and pertinent spectroscopic data) of the indicator used in the experiment, and then give the calculated pK_a for the indicator system.

On the second page of the reports answer the following questions, giving a clearly thought-out explanation of each answer.

- 1) What single error would have the greatest effect on the accuracy of the experimental results?
- 2) All indicator pK_a values in this experiment are within 2 units of the pK_a of acetic acid. Is this necessary to the method, or can any indicator pK_a be determined in acetate buffer solutions?