Spectrophotometric and Potentiometric Determination of pH

Introduction

Determination of pH is one of the most frequently performed measurements in chemistry. The potentiometric method with a glass electrode has been widely used for pH measurements but has drawbacks such as the need for a reference electrode, susceptibility to electrical interference, instrument drift, and the need for physical contact with the solution. It is desirable to have alternative methods for pH determination. One such method is spectrophotometric measurement with the use of a suitable pH indicator.

In the spectrophotometric method used here, the pH of an unknown solution is determined by addition of a small amount of a pH indicator and determination of the extent of dissociation of the indicator (a weak acid). Because overlap exists between the spectra for the acid form (generically represented as HIn) and base form (In^-) of the indicator, it is necessary to determine individual molar absorptivities for each form at two wavelengths (λ_1 and λ_2). Usually these are the wavelength peaks (absorption maxima) of HIn and In^-. Assuming that the absorbances of the two forms are additive (independent of one another), we obtain two simultaneous linear equations for the absorption at the two wavelengths measured:

$$A_1 = \varepsilon_1^{HIn}\, b\, [HIn] + \varepsilon_1^{In^-}\, b\, [In^-] \qquad (1a)$$

$$A_2 = \varepsilon_2^{HIn}\, b\, [Hin] + \varepsilon_2^{In^-}\, b\, [In^-] \qquad (1b)$$

where b is the pathlength (usually 1 cm),

A_1 and A_2 are the absorbances at λ_1 and λ_2,

ε_1^{HIn} and ε_2^{HIn} are the molar absorptivities of HIn at λ_1 and λ_2, and

$\varepsilon_1^{In^-}$ and $\varepsilon_2^{In^-}$ are the molar absorptivities of In^- at λ_1 and λ_2.

The molar absorptivities ε_1^{HIn} and ε_2^{HIn} can be determined from the absorbance of the indicator prepared in an acidic solution where $[In^-] \sim 0$. Similarly, $\varepsilon_1^{In^-}$ and $\varepsilon_2^{In^-}$ can be determined from the absorbances of the indicator prepared in a basic solution where

[HIn] ~ 0. In an unknown solution, the [HIn] and [In^-] can be calculated from A_1 and A_2 by solving the two equations (1a and 1b). The unknown buffer's [HIn] and [In^-] and the solution's ionic strength may then be used to calculate the corresponding activities a_{HIn} and a_{In^-} that can then be used in the Henderson-Hasselbalch expression to find the pH.

In this experiment, the pH indicator bromocresol green (K_a = 1.60 x10^{-5}) will be used for the spectrophotometric procedure – you will need to look this indicator up to find out which two conjugate species are present in aqueous solution at pH ~ 4.8, since their charges need to be known for the activity correction. The pH of an acetate buffer will be determined by both spectrophotometric and potentiometric methods and the results will be compared. In the Introduction section of your report, you should briefly discuss why bromocresol green is a suitable indicator for this experiment.

Apparatus

plastic cuvette (1)
100 mL volumetric flask (1)
50 mL volumetric flasks (3)
5 and 10 mL pipets (1 each)

Instrumentation (See Appendices for Operating Instructions)

WPA Biowave II or comparable benchtop UV-Visible spectrophotometer
Digital pH meter and pH electrode

Solutions available

(1) Standard pH calibration buffer solutions (pH = 4.00 and pH = 7.00)
(2) 1.0 x10^{-4} M bromocresol green (measure out about 75 mL with a graduated cylinder)
(3) 0.10 M HCl
(4) 0.10 M NaOH
(5) 2.40 M acetic acid

Solution to be prepared

Buffer solution: Pipet 5.00 mL of 2.40 M acetic acid into a 100 mL volumetric flask and dilute with about 50 mL of deionized water. Weigh about 0.825 g (to 0.001 g) of sodium acetate ($NaC_2H_30_2$, FW = 82.03) and quantitatively transfer to the same volumetric flask and dissolve completely. Finally, fill the flask to the mark with deionized water and mix thoroughly. Calculate and record the analytical concentrations of the acetic acid and acetate.

Procedure

(1) Preparing the sample solutions for the spectrophotometric method

Pipet 10 mL of the bromocresol green solution to each of three 50-mL volumetric flasks. Use a graduated cylinder to add 25 mL of 0.10 M HCl, 0.10 M NaOH, and the buffer solution, respectively. Dilute to the mark with deionized water and mix thoroughly.

(2) Measuring the baseline

Rinse the cuvette with tap water and deionized water, fill it with deionized water, and place it in the holder. Set up the spectrophotometer and measure the "baseline" using the deionized water.

(3) Measuring the spectra of the three solutions

Rinse the cuvette with a sample solution twice, fill it with the solution, place it in the holder, and measure the spectrum. Measure the spectra of all three solutions, *i.e.*, acidic, basic, and buffer. If you wish, you can check for spectrometer drift or alignment problems by thoroughly rinsing the cuvette and remeasuring the spectrum of the deionized water (the *blank*).

(4) Reading the absorbance

Locate the peak wavelengths at the absorption maxima of the acidic and basic solutions (*i.e.*, for Hln and In^-). Write down the peak wavelengths in your notebook. Then read and record the absorbance at THESE TWO PEAK WAVELENGTHS FOR ALL THREE SOLUTIONS. (Please note that the peak wavelengths of the buffer solution may be slightly different from the ones of the acidic and basic solutions, but you MUST read the absorbance of the buffer solution at the peak wavelengths of the acidic and basic solutions.) Download or manually record enough wavelength points for the three spectra that you can reconstruct them in Excel or some other suitable graphing program.

(5) Measuring pH with a glass electrode

Calibrate the pH meter with the two standard buffers - pH 7.00 and pH 4.00. Measure the pH of the unknown buffer solution.

Report: A minor report is required for this experiment (50 points): in preparing it, you should consider/complete/discuss the following:

(1) Tabulate the absorbances (at your two chosen peak wavelengths) of the acidic solution, basic solution, and the buffer. Make corrections to the absorbances if necessary (based on a final measurement of the blank), but be sure to explain any corrections in the Discussion section of your report. Calculate and report the molar absorptivities of Hln and In^- at the two wavelengths. Calculate [Hln] and [In^-] and the corresponding activities in the buffer. Calculate the pH of the buffer solution using the K_a given above. Remember that the spectrophotometric method measures the concentrations of the two indicator forms, so you will need some way of calculating the activity coefficient for any ions involved (*e.g.*, the Debye-Huckel equation). Don't forget that the ionic strength of the solution is primarily determined by the major components of the buffer. Be sure to report what you end up using for the ionic strength and the activity coefficient and briefly explain how you obtained them.

(2) Report the pH measurement by the potentiometric method with a glass electrode. (Remember that the potentiometric method directly measures the activity of H^+ *i.e.*, pH = -log a_{H+} so no activity corrections are needed.)

(3) Note that a purely theoretical value for the pH of the buffer can also be calculated from the presumed activities (*i.e.*, activity adjusted analytical concentrations) of acetic acid (HOAc) and acetate (OAc^-) using the correct form of the Henderson-Hasselbalch equation, pH = pK_a + log(a_{OAc^-}/a_{HOAc}). Calculate and report the pH obtained in this way, again being careful to specify how activities were obtained. It is also interesting to calculate the pH based on the analytical concentrations (without activity corrections) to compare to the proper value.

(4) Compare the pH values obtained by the three methods: spectrophotometry, potentiometry, and the Henderson-Hasselbalch equation using analytical concentrations and activities. Discuss the agreement and/or differences among the pH values obtained by the different methods. Are the results consistent with one another? Are they what you expected to get? Why would one method be expected to be superior or inferior to the others?

(5) Discuss the advantages and disadvantages of spectrophotometric and potentiometric methods of determining pH in some real-world measurement situations. (It isn't hard to imagine some real-world situations where the pH would need to be known. It's a bit more of a stretch to imagine a situation where the pH electrode would be a problem.)

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