

Buffer Solutions

Introduction

This experiment demonstrates another method of determining the dissociation constant for a weak acid. The acidity constant of a solution of a weak acid is defined as:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

where $[A^-]$ is the concentration of the conjugate base and $[HA]$ that of the undissociated acid. Solving for $[H^+]$, then taking the negative logarithm (base 10) gives:

$$pH = pK_a - \log \frac{[HA]}{[A^-]}$$

where the pH is $-\log[H^+]$ and pK_a is $-\log K_a$. This equation assumes that the activity coefficients are unity for all of the species involved in the equilibrium, as should be the case for sufficiently dilute solutions. For solutions that are not infinitely dilute, the activity coefficients of the ions are not unity, but may be approximated using the Debye-Hückel limiting law (see experiment 5). Thus, we may express the thermodynamic equilibrium constant (K) as a function of the ionic strength of the solution:

$$\log K_a = \log K + 1.018I^{\frac{1}{2}}$$

where I is the ionic strength. By measuring the pH of a dilute solution of a weak acid as it is being titrated with a strong base, we may determine the equivalence point (where the acid has been neutralized), and from this, the pH at the point where the acid and conjugate base are equimolar, which will be equal to the pK_a .

Procedure

Prepare 250 mL each of solutions having acid concentrations of 0.05, 0.025, 0.0125, 0.00625 M (the instructor will assign one monoprotic weak acid and one diprotic weak acid to each group). Once prepared, these should be stored in a 25°C water bath. Prepare 250 mL solutions of NaOH (from the standardized stock solution) that will allow you to neutralize 30 mL of acid solution with between 10 and 30 mL of base. These solutions should also be stored in the water bath until their use.

Transfer 30 mL of acid solution to a beaker, immersing the pH electrode, and stirring with the magnetic stirrer. Record the pH of the acid solution. Titrate the solution by

adding a measured amount of the appropriate NaOH solution from the buret, recording the pH after each addition. Continue until clearly beyond the equivalence point. Repeat this procedure three times for each acid solution concentration, remembering to rinse the buret thoroughly when changing the base concentration. After performing these titrations, repeat the procedure for the diprotic acid.

Calculations

Determine the K_a values for the monoprotic acid at each concentration from the pH of the pre-titrated solution and that of the solution at after addition of one-half of the base necessary for neutralization. Plot $\log K_a$ versus $I^{1/2}$, the intercept should be equal to the logarithm of the thermodynamic equilibrium constant K . Compare this value to the literature value. Repeat this procedure for the diprotic acid.