Thermodynamics of Acid–Base and Complex Equilibria

Measurement of pK for Weak Bases with the Aid of Sodium Ion-Selective Electrodes

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A method for obtaining pK_a of weak bases from emf measurements of cells with glass pH electrodes and sodium ion-selective electrodes is described. The Harned–Ehlers method [1] uses hydrogen and Ag/AgCl electrodes; it yields accurate results but requires special apparatus and techniques and numerous data. The present method produces somewhat less accurate data; it retains the advantages of a cell with liquid junction, however, and is both simple and rapid. It is particularly suited to the study of bases where the solubility of AgCl is often of concern.

To determine the equilibrium constant K_a for the process $BH^+ \rightleftharpoons B + H^+$, one measures the emf (E) of cells

$$\begin{array}{c|c|c} \text{pH glass} & & \\ \text{electrode} & BH^+(m_1), B(m_2), NaCl(m_3) & \text{Na ISE} \end{array}$$

The emf of this cell is given by

$$pK_a + \log(\gamma_{Na^+}\gamma_B/\gamma_{BH^+}) = \\ = (E-E^\circ)/k + \log(m_{BH}/m_B m_{Na})$$

where k is the Nernst slope, 2.3026 RT/F. With weak bases ($K_b < 10^{-4}$) and a fixed small molality of Na^+ (*e.g.*, 0.01 *m*), the last term remains constant when the buffer is diluted with NaCl solution. More important, the activity coefficient term is small and varies linearly with ionic strength (I). Thus E is a linear function of I, with a small slope. This is not the case with the Harned method, where this term is log $(\gamma_{BH^+}\gamma_{Cl^-}/\gamma_B)$.

The value of pK_a can be derived from the intercept (E′) at I = 0. Similar measurements of E′ for a reference base of known pK_a (*e.g.*, tris(hydroxymethyl)aminomethane [2]) provide the value of E°. If the buffer ratio and sodium molality are the same for the reference buffer and the unknown buffer, $\Delta pK_a = \Delta E'/k$.

Results are given for several weak bases in water and in 50% methanol/water at temperatures from 15 to 35 °C. The responses of the electrodes were in accord with the Nernst slope. Two or three measurement were sufficient to yield values of pK_a. The results agreed well with accepted constants from the literature.

References

1 H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc., 54,* 1350 (1932).

2 R. G. Bates and H. B. Hetzer, *J. Phys. Chem., 65,* 667 (1961).

Formation and Stability of Alkali-Metal Complexes of Some Carboxylic and Hydroxycarboxylic Acids in Aqueous Solution

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Alkali-metal ions form weak complexes with various low-molecular-weight organic ligands [1]. Most of these ligands are of biological interest and are present both in biofluids and in natural waters. Since a large amount of alkali-metal ions is present in all natural fluids (*e.g.* sodium and potassium are the main ionic constituents of all intra- and extracellular liquids and play a fundamental role in electrical communication through membranes), the knowledge of the formation constants of their complexes is quite important. Furthermore, the comparison of the stability constants concerning complexes of other metal ions, determined in different ionic media (in particular K^+ and Na^+), can give rise to some uncertainties if the formation constants of the alkali-metal complexes are unknown.