3.1 pK_a and Ionizable Substances

The definition of $pK_{(a)}$ and pk_a have been discussed in chapter 2. For substances that are carboxylic acids (HA) it is advantageous to determine the pK_a, since this property is of importance in a series of considerations. For carboxylic acid the species A^- usually absorbs in the ultraviolet (UV) region, and its concentration can be determined spectrophotometrically (Underberg and Lingeman, 1983); HA on the other hand will absorb at a different wavelength.

The molar absorbances of the two species at a given wavelength are denoted ε_0 and ε_- (it is assumed that at the wavelength chosen $\varepsilon_0 < \varepsilon_-$), and it can be shown that if the solution is m_0 Molar in total A, then

$$\frac{A^-}{HA} = \frac{\varepsilon - \varepsilon_0 m_0}{m_0\varepsilon_- - \varepsilon} \tag{9.1}$$

so that the ratio A^-/HA can be determined in a series of buffers of different pH. Hence the $pK_{(a)}$ can be found as the intercept by plotting pH as a function of $\log[(A^-)/(HA)]$ by Henderson–Hasselbach:

$$pH = pK_{(a)} + \log\left[\frac{A^-}{HA}\right] \tag{9.2}$$

If several buffer concentrations are used, extrapolation can be carried out to zero ionic strength, and the pK_a can be determined. For initial studies, however, a $pK_{(a)}$ in the correct range (i.e., $+0.2$ unit) will suffice, so that the determination above can be done at one buffer concentration only.

The conventional approach is to do titrations (Fig. 1), and this will yield graphs of fraction (neutralized (x) as a function of pH. Usually, the water is titrated as well (Parke and Davis, 1954), and what is presented in Fig. 1 is the "different." The $pK_{(a)}$ is then the pH at half neutralization (which is also the inflection point).

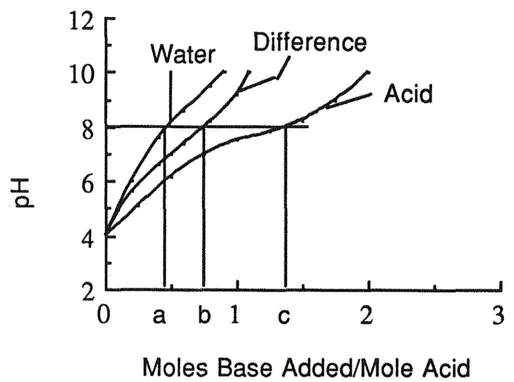

Fig. 1 Typical titration curves. The "water" curve indicates the amount of alkali needed to "titrate" the water, and the "acid" curve is a conventional titration curve. The difference curve is the horizontal difference between the "acid" and the "water" curve and is the adjusted titration curve. For example the point "b" is "c" minus "a". The $pK_{(a)}$ is the point of inflection, which is also the point where half of the acid is neutralized.