## E17 Acid Ionisation Constant of Acetic Acid from Titration Curve

## Abstract

The acid ionisation constant for acetic acid has been determined by titration with NaOH . The $\mathrm{p} K_{\mathrm{a}}$ value is found to be 4.6 in good agreement with the literature value.

## Introduction

When weak acids such as acetic acid dissolve in water, they only dissociate to a small extent. For acetic acid, $\mathrm{CH}_{3} \mathrm{COOH}$, the dissociation reaction is:

$$
\begin{equation*}
\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq}) \tag{1}
\end{equation*}
$$

For this reaction, the equilibrium constant is also known as the acid ionisation constant, $K_{\mathrm{a}}$ :

$$
\begin{equation*}
K_{\mathrm{a}}=\frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})\right]\left[\mathrm{H}^{+}(\mathrm{aq})\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})\right]} \tag{2}
\end{equation*}
$$

The aim of this experiment is to determine the value of $K_{\mathrm{a}}$ for acetic acid and to evaluate the accuracy of titrations in measuring it. It is commonly tabulated using the $\mathrm{p} K_{\mathrm{a}}$ where:

$$
\begin{equation*}
\mathrm{p} K_{\mathrm{a}}=-\log _{10} K_{\mathrm{a}} \tag{3}
\end{equation*}
$$

Equation (2) can be re-arranged to give:

$$
\begin{equation*}
\left[\mathrm{H}^{+}(\mathrm{aq})\right]=K_{\mathrm{a}} \times \frac{\left[\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})\right]}{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})\right]} \tag{4}
\end{equation*}
$$

If a dilute solution of acetic acid is titrated with a dilute solution of sodium hydroxide, the following reaction occurs:

$$
\begin{equation*}
\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \rightarrow \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \tag{5}
\end{equation*}
$$

During the titration, $\left[\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})\right]$ decreases and $\left[\mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-}(\mathrm{aq})\right]$ increases. From equation (3), this leads to a continuously decreasing value of $\left[\mathrm{H}^{+}(\mathrm{aq})\right]$. This can be measured through the increase in the pH . At the point when enough NaOH has been added that $\left[\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})\right]=\left[\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})\right]$, equation (4) predicts that $\left[\mathrm{H}^{+}(\mathrm{aq})\right]=K_{\mathrm{a}}$. At the equivalence point, the NaOH added has reacted with all of the acetic acid. $\left[\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})\right]=\left[\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}(\mathrm{aq})\right]$ occurs when half of this volume has been added. It is called the half-equivalence point. The pH at this point should equal the $\mathrm{p} K_{\mathrm{a}}$ value for acetic acid. A plot of pH against the amount of added NaOH is called a titration curve.

## Method

The method in the laboratory handbook ${ }^{1}$ on pages E17-6 to E17-10 was followed.

## Results

Figure 1 shows the titration curve obtained in this experiment.
The equivalence point is the mid-point on the vertical part of the curve. It corresponds to a volume of NaOH of 26 mL and a pH of 8.57. The half equivalence point corresponds to a volume of 13 mL and a pH of 4.6. The value of $K_{\mathrm{a}}$ from the titration is 4.6.


Figure 1. Titration curve showing the changes in pH when 0.1 M NaOH is added to 50 mL of a 0.05 M acetic acid solution.

## Discussion

The titration curve follows that expected for the titration of a weak acid with a strong base ${ }^{2}$. The initial pH is 2.95 and is significantly higher than that for a strong acid of the same concentration. After addition of some NaOH , the curve is relatively flat where $\left[\mathrm{H}^{+}(\mathrm{aq})\right]$ is given by equation (2). Near the equivalence point, the pH rises sharply. At the equivalence point, all of the $\mathrm{CH}_{3} \mathrm{COOH}$ has reacted and the solution contains $\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}$. The pH at this point is greater than 7 as the acetate ion is a weak base and undergoes hydrolysis.

At the half equivalence point, $\left[\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})\right] /\left[\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})\right]=1$ and $\mathrm{pH}=\mathrm{p} K_{\mathrm{a}}$. The titration curve gives the value of 4.6. The experimental value is in reasonably good agreement with the literature value ${ }^{3}$ of 4.76 . The experimental value is slightly lower, perhaps because the exact equivalence point was missed during the titration. It is also possible that the solution was slightly more acidic than expected due to dissolved $\mathrm{CO}_{2}$. To improve the result, the experiment could be repeated a number of times to find a better value for the equivalence point and the water could be boiled to remove dissolved $\mathrm{CO}_{2}$.

## Conclusions

From the titration of acetic acid with NaOH , its $\mathrm{p} K_{\mathrm{a}}$ value is 4.6 . This is in reasonable agreement with the literature value of 4.76. This indicates that titration curves are a good method of determining acid dissociation constants.

## References

1. First Year Chemistry Laboratory Handbook, The University of Sydney, Australia, 2009.
2. Blackman, A., Bottle, S., Schmid, S., Mocerino, M. and Wille, U., Chemistry, Wiley, Australia, 2008, Section 11.7.
3. Acid Dissociation Constant, Wikipedia, http://en.wikipedia.org/wiki/Acid_dissociation_constant, accessed 09/04/09.
