EXPERIMENT 2
DETERMINATION OF $K_a$ USING THE CONDUCTANCE METHOD

Introduction

Equilibrium Processes

When a pure sample of liquid-state acetic acid (i.e., CH$_3$COOH$_{(l)}$/HAc$_{(l)}$) is added to a beaker of pure water, at least two significant processes occur. First, the acetic acid (assuming it to be the solute) will dissolve completely in the water (assuming it to be the solvent). As acetic acid is infinitely soluble in water (i.e., the two liquids are miscible), this process of dissolution will result in a solution of acetic acid and water with no measurable amount of pure solute. As this process has proceeded completely, (i.e., 100%) an equilibrium expression need not be considered. Second, the dissolved acetic acid will undergo the process of dissociation, a process which may be represented by an equilibrium expression and which is the focus of this lab. Both processes may be expressed symbolically:

$$\text{CH}_3\text{COOH}_{(l)} \xrightarrow{\text{H}_2\text{O}_{(l)}} \text{CH}_3\text{COOH}_{(aq)} \rightleftharpoons \text{CH}_3\text{COO}^-_{(aq)} + \text{H}^+_{(aq)}$$

When acetic acid dissociates, a proton is liberated, and therefore the equilibrium constant representing this process is referred to as the acid dissociation constant ($K_a$).

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \times \frac{\gamma_{(\text{H}^+)\gamma_{(\text{CH}_3\text{COO}^-)}}}{\gamma_{(\text{CH}_3\text{COOH})}} \quad [1]$$

where the parameter $\gamma$ is defined as the activity coefficient of that particular substance.

Conductance

A very common method to use when determining the acid dissociation constant of a sample is called the conductance method, as one measures the conductance of a solution. Conductance, $G$, (SI unit is the siemens, S, where 1 S = 1 Ω$^{-1}$) is defined as the reciprocal of resistance and can be understood to represent the ease with which electrical current flows through a given substance. With regards to our setup, the conductance is seen to be proportional to the electrode surface area, $A$, and inversely proportional to the distance between the electrodes, $l$:

$$G = \kappa \frac{A}{l} \quad [2]$$

where $\kappa$ is the conductivity ($\mu$S cm$^{-1}$) of the solution. The conductivity parameter depends upon (i) the equivalent concentrations, (ii) the charge numbers and (iii) the mobilities of the ionic species present. An additional parameter, $\alpha$, representing the fractional ionization at a given solute concentration is now introduced and is related to conductivity:

$$\kappa = 1000 \text{Cav} \mathcal{F}(U_+ + U_-) \quad [3]$$

where:
C is the concentration of the solute in solution. (mol L⁻¹)

ν is the simplified form of a parameter which represents the number of equivalents and the charge numbers of positive and negative ions per mole of electrolyte and is equal to 1 for any 1:1 electrolyte.

F is the Faraday constant. (C equiv⁻¹)

U± are the ionic mobilities for the positive and negative ions (in m² s⁻¹ V⁻¹)

By rearranging [3], one obtains the equivalent conductance, Λ (Ω⁻¹ cm² equiv⁻¹). This form is useful as it eliminates the need to worry about ionic mobilities and charges. Please note that this is a simplification and may be applied only to 1:1 electrolytes. The equivalent conductance is defined as:

\[
Λ = \frac{k}{1000C} = \alpha F(U_+ + U_-)
\]  

[4]

For this system, it is assumed that the fractional ionization is approximated by the ratio of equivalent conductance at a given concentration to that at infinite dilution:

\[
\alpha = \frac{Λ}{Λ_0}
\]  

[5]

For strong electrolytes, Λ varies only slightly with concentration (as α does not vary), and Λ₀ can be determined by measuring Λ at various solute concentrations:

\[
Λ = Λ_0(1 - \epsilon \sqrt{C})
\]  

[6]

where ε is a proportionality constant. Thus, a plot of Λ against \(\sqrt{C}\), followed by extrapolation to infinite dilution, will produce Λ₀. For weak electrolytes, Λ is no longer nearly constant (as α varies markedly with concentration) and Λ₀ must be determined using an indirect approach, which relies upon the equivalent conductances of several strong electrolytes at infinite dilution (The Kohlrausch method):

\[
Λ_0(\text{HAc}) = Λ_0(\text{HCl}) + Λ_0(\text{NaAc}) - Λ_0(\text{NaCl})
\]  

[7]

Relating Conductance Measurements to Dissociation Constants

Recalling that C represents the concentration of the undissociated acetic acid and α represents the fractional dissociation of acetic acid, it is understood that:

\[
[H^+] = [\text{CH}_3\text{COO}^-] = αC
\]  

[8]

This modifies [1] in the following manner:

\[
K_a = \frac{α^2C}{(1 - α)} \times \frac{γ_{H^+}γ_{\text{CH}_3\text{COO}^-}}{γ_{\text{CH}_3\text{COOH}}}
\]  

[9]
Recalling the definition of fractional dissociation in terms of equivalent conductances, the above equation modifies to:

\[ K_a = \frac{\Lambda^2 C}{\Lambda_0 (\Lambda_0 - \Lambda)} \times \frac{\gamma_{H^+} \gamma_{CH_3COO^-}}{\gamma_{CH_3COO}} \]  \[10\]

Let the right hand portion of [10] which does not contain activity coefficients equal the dissociation function, \( K_c \), which is a quantity related to the true acid dissociation constant. As undissociated acetic acid is necessarily non-electrolytic, its activity coefficient equals unity and may be disregarded. Also, as all solutions are of relatively low solute concentration, one may use the Debye-Hückel limiting law to give:

\[ \log K_a = \log K_c - 1.018\sqrt{C} \alpha \]  \[11\]

By determining the dissociation function for a number of acetic acid solutions of low concentration and by plotting \( \log(K_c) \) versus \( \sqrt{C} \alpha \) with linear extrapolation to \( C = 0 \), one can determine the acid dissociation constant, \( K_a \), at that particular temperature.

**The Dissociation Constant as a Function of Temperature**

The acid dissociation constant may be treated just like any other equilibrium constant and thus its variation with changing temperature obeys the *van't Hoff equation*, which takes the form below after it is integrated:

\[ \ln K_{a_2} - \ln K_{a_1} = \frac{-\Delta_d H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]  \[11\]

It is assumed that the enthalpy of dissociation, \( \Delta_d H \), is constant over the temperature range, \([T_1, T_2] \).
Materials

- 3 – 250 mL volumetric flasks
- 1 – 100 mL graduated cylinder
- 1 – 50 mL graduated cylinder
- 5 – 100 mL beakers
- 1 – 250 mL beaker
- Vernier with conductance probe
- hydrochloric acid (HCl)
- acetic acid (CH₃COOH)
- sodium acetate (CH₃COONa)
- sodium chloride (NaCl)

Procedure

The following stock solutions will be provided:
1. 0.1 M sodium chloride (NaCl)
2. 0.1 M sodium acetate (CH₃COONa)
3. 0.04 M hydrochloric acid (HCl)
4. 0.02 M acetic acid (CH₃COOH)

A. Preparation of Required Solutions
1. Each stock solution provided will be used to make three dilute solutions, each 250 mL in volume. In addition, keep about 50 mL of the stock solution in a labelled 100 mL beaker. All required solution concentrations are outlined in Table 2.1 (Note: prepare only one set of solutions at a time - only use deionized water, do not use tap water).

<table>
<thead>
<tr>
<th>Set</th>
<th>Compound</th>
<th>Concentrations (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaCl</td>
<td>0.02, 0.04, 0.08, 0.10</td>
</tr>
<tr>
<td>2</td>
<td>CH₃COONa</td>
<td>0.02, 0.04, 0.08, 0.10</td>
</tr>
<tr>
<td>3</td>
<td>HCl</td>
<td>0.005, 0.01, 0.02, 0.04</td>
</tr>
<tr>
<td>4</td>
<td>CH₃COOH</td>
<td>0.004, 0.008, 0.01, 0.02</td>
</tr>
</tbody>
</table>

B. Calibration of the Conductivity Probe (repeat steps as required)
1. Make sure the computer console has been turned on and that the conductivity probe has been correctly connected. Please ask a TA for help if this has not yet been done.
2. Load the Logger Pro software and make sure that the conductivity probe is set to the 0 – 20000 µS range if using a strong electrolyte or the 0 – 2000 µS range if using a weak electrolyte. The switch controlling the range is found on the black conductivity probe box.
3. Rinse the probe with de-ionized water (do not scratch the electrodes!) and dry the outside with a delicate task wiper (i.e., a Kimwipe).
4. Load an appropriate calibration file, which can be found under the “Experiments/Probes & Sensors/Conductivity” directory. Note: consider the conductivity range you are using. This calibration file will automatically setup the probe for use. Make note of this conductivity
reading ("the air reading") as it must be subtracted from all subsequent measurements.

5. As a quick check of the probe, (perform only once) add about 50 mL of de-ionized water to a 100 mL beaker and about 50 mL of tap water to another 100 mL beaker. Take the conductivity measurements of both solutions. The de-ionized water reading should be equal or very close to the air reading, while the tap water reading should be much different. Also, using the Vernier temperature probe, measure and then record the temperature of one of the solutions into your data sheet.

C. Conductivity Measurements

1. Once a set of solutions has been prepared and making sure that the probe has been correctly calibrated, add about 50 mL of each diluted solution to a labelled 100 mL beaker. A 250 mL beaker has been provided to use as a quick rinse and should be prepared with fresh de-ionized water for each set of solutions. **For acetic acid:** the de-ionized water should be changed after each measurement.

2. Dip the conductivity probe into the solution (see Figure 2.1) with the lowest electrolyte concentration and click on the **Collect** button, which can be found near the top right of the screen. This will start the data acquisition process and produce a plot on the screen.

3. Once the reading has stabilized (ca. 10 s), record the value on your data sheet, remove the probe from the solution, blot dry, swirl in the de-ionized water bath, blot dry again and dip the probe into the solution having the next highest electrolyte concentration.

4. Repeat step 3 until the conductivities of all the solutions in a set have been recorded.

5. Clean all glassware (beakers, flasks, etc.) and move on to the next set of solutions.

6. After the conductivities of all 16 solutions (4 sets of 4 solutions) have been measured, perform a final cleaning of the conductivity probe, exit the Logger Pro program and return all glassware to the appropriate student locker.

Figure 2.1
Calculations

1. Using equation [4], determine \( \Lambda \) values for all of the solutions that contain a strong electrolyte. The cell constant, \( A/l \), is equal to 1 cm.

2. Plot \( \Lambda \) vs. \( \sqrt{C} \) and determine \( \Lambda_0 \) for all the strong electrolytes.

3. Using the Kohlrausch method, evaluate \( \Lambda_0 \) for acetic acid.

4. For each acetic acid solution, determine \( \Lambda, \alpha, \) and \( K_c \), and present these findings in a table.

5. By plotting \( \log(K_c) \) vs. \( \sqrt{C \alpha} \) and extrapolating to \( C = 0 \), find \( pK_a \) for the temperature at which the experiment was conducted.

6. Determine the enthalpy of dissociation, \( \Delta_dH \), for acetic acid under standard conditions.

7. Using [12], determine \( K_a \) under standard conditions and compare your findings with the literature. Note: the value of \( K_a \) for acetic acid is incorrect in both Atkins 7th and 8th editions, though the listed \( pK_a \) is correct.

Lab Questions

1. Why, when determining \( \Lambda_0 \) for a weak electrolyte, it is preferable to determine the equivalent conductance at infinite dilution for several strong electrolytes as opposed to determining it directly using the weak electrolyte?

2. Using the Debye-Hückel-Onsager limiting law, compute the ionic molar conductivity for \( \text{Zn}^{2+}(\text{aq}) \) and \( \text{SO}_4^{2-}(\text{aq}) \) ions in a 0.01 molar aqueous solution of \( \text{ZnSO}_4 \) at 298.15K. The limiting ionic molar conductivities are \( \lambda(\text{Zn}^{2+}) = 105.6 \text{ S cm}^2 \text{ mol}^{-1} \) and \( \lambda(\text{SO}_4^{2-}) = 160.0 \text{ S cm}^2 \text{ mol}^{-1} \). Use your results to calculate \( \Lambda(\text{ZnSO}_4) \) at the given concentration. Calculate the percent error in your result by comparison to the result in the CRC Handbook.

3. You should have noticed that, at the end of the experiment, only a small fraction of the total solution made was actually utilized for conductance measurements. Why were such large amounts of solution prepared when only a small portion was used?

4. When the sample under study is a non 1:1 weak electrolyte, explain why the definition of equivalent conductance, as outlined earlier, no longer holds.

5. The molar conductivity of an aqueous 0.10 molar solution of \( \text{AgNO}_3 \) is 109.09 S cm\(^2\) mol\(^{-1}\) at 298.15K. When this solution is placed in a particular conductance cell, the resistance of the solution is found to be 35 \( \Omega \). Compute the specific conductivity of the \( \text{AgNO}_3 \) solution.

References


Data Sheet

Temperature of solutions: _______ °C
Concentration of CH₃COOH solution: ________ mol L⁻¹
Concentration of HCl solution: ________ mol L⁻¹
Conductivity reading of air using: (i) 0 – 2000 µS cm⁻¹ range ____________ µS cm⁻¹
   (ii) 0 – 20000 µS cm⁻¹ range ____________ µS cm⁻¹

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<tr>
<th>#1 - NaCl</th>
<th>#2 - CH₃COONa</th>
<th>#3 - HCl</th>
<th>#4 - CH₃COOH</th>
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