valid for academic year 2018/2019

CONDUCTOMETRIC AND POTENTIOMETRIC DETERMINATION OF THE DISSOCIATION CONSTANT OF A WEAK ACID

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Place of exercise: Department of Physical Chemistry and Technology of Polymers; room 210/c

PHYSICAL CHEMISTRY LABORATORY
I. **Aim of the exercise**

The goal of this exercise is to familiarise students with the practical approach to electrolytic dissociation and conductometric measurements. During the exercise, the students should apply the knowledge, gained during earlier physical chemistry courses, to determine the dissociation constant of a weak acid. This will be based on a series of resistance measurements of solutions with a varying concentration of a weak acid.

II. **Introduction**

1. **Dissociation constant of a weak acid**

Upon dissolution of a weak acid (HA) in water (or any other solvent), it undergoes electrolytic dissociation, producing ions. Dissociation does not occur quantitatively and a certain equilibrium is achieved, as described by the following equation:

$$\text{HA} + \text{H}_2\text{O} \Leftrightarrow \text{H}_3\text{O}^+ + \text{A}^-$$  \hspace{1cm} (1a)

which can be simplified to:

$$\text{HA} \Leftrightarrow \text{H}^+ + \text{A}^-$$  \hspace{1cm} (1b)

The Guldberg-Waage (law of mass action) law applies to this equilibrium, therefore:

$$K = \frac{a_{\text{H}^+} \cdot a_{\text{A}^-}}{a_{\text{HA}}}$$  \hspace{1cm} (2)

Where:

- a – are the equilibrium activities of ions (H\(^+\), A\(^-\)) and undissociated molecules (HA),
- K – is the electrolytic dissociation constant of the weak acid.

Expressing the activity of each ion as the product of its concentration (C\(_i\)) and its activity coefficient (f\(_i\)), we obtain Equation 3:

$$K = \frac{c_{\text{H}^+} \cdot c_{\text{A}^-} \cdot f_{\text{H}^+} \cdot f_{\text{A}^-}}{c_{\text{HA}} \cdot f_{\text{HA}}}$$  \hspace{1cm} (3)
Denoting the dissociation degree as $\alpha$, we can write Eq. 3 in the following form:

$$K = \frac{\alpha^2 \cdot C_0 \cdot f_{H^+} \cdot f_{A^-}}{1 - \alpha \cdot \frac{f_{HA}}{f_{H^+}}}. \quad (4)$$

Where:

$C_0$ – is the analytical concentration of the acid.

In the case of dilute solutions of weak electrolytes ($K<10^{-5}$), we can estimate that the activity coefficients are equal to one, allowing the above equation to be simplified to the form present in the formulation of Ostwald’s dilution law:

$$K^* = \frac{\alpha^2 \cdot C_0}{1 - \alpha}. \quad (5)$$

Following the reasoning of Arrhenius, that the dissociation constant of an acid of a given concentration is equal to the ratio of its equivalent conductivity ($\Lambda$) to its limiting equivalent conductivity in an infinitely dilute solution ($\Lambda^0$):

$$\alpha = \frac{\Lambda}{\Lambda^0}. \quad (6)$$

The concepts of gram equivalent (equivalent weight) and equivalent concentration (normality) are practically not in use for many years, in exchange mole and molar concentration are currently used. As a result, the equivalent conductivity $\Lambda$ [m²·Ω⁻¹·g-equiv.⁻¹] is replaced with molar conductivity $\Lambda_m$ [m²·Ω⁻¹·mol⁻¹]. Eq. 6 is then written in the following form:

$$\alpha = \frac{\Lambda_m}{\Lambda^0_m}. \quad (7)$$

Combining Eq. 7 with Eq. 5, we obtain the following:

$$K^* = \frac{\Lambda_m^2 \cdot C_0}{\Lambda^0_m \left(\Lambda^0_m - \Lambda_m\right)}. \quad (8)$$
Therefore, by measuring the molar conductivity of an electrolyte solution with a given concentration and knowing its limiting molar conductivity, Eq. 8 can be used to determine the classical dissociation pseudo-constant (K*).

The investigation of dilute solutions of weak acids by this method produces dissociation constant values approximately equal to those obtained using more precise methods. If the K* is greater than 10^{-5}, however, it is absolutely necessary to take into account the activity coefficients:

\[ K = K^* \cdot \frac{f_{H^+} \cdot f_{A^-}}{f_{HA}} = K^* \cdot f^2_{\pm} \]  

Where:

\( f_\pm \) – is the average activity coefficient for ions in the investigated solution.

The average activity coefficient for ions in the electrolyte solution is calculated using the boundary Debye – Hückel equation:

\[ \log(f_\pm) = -A \cdot |z_+| \cdot |z_-| \cdot \sqrt{I} \]  

Where:

\( A \) – is an experimental coefficient, whose value is determined for a given temperature, for the medium in which measurements are carried out,

\( z_+, z_- \) – are the charges of the respective ions, constituting the investigated electrolyte,

\( I \) – is the ionic strength of the electrolyte solution.

Taking the logarithm of Eq. 9, we obtain:

\[ \log(K) = \log(K^*) + 2 \cdot \log(f_{\pm}) \]  

Substituting the value of the average activity coefficient, calculated from the above into Eq. 10, we obtain:
\[
\log(K) = \log(K^*) - 2 \cdot A \cdot |z_+| |z_-| \cdot \sqrt{I}
\]  \hspace{1cm} (11b)

The ionic strength of an electrolyte solution is a function of the concentration and charge of all the ions present in the solution, according to the following:

\[
I = \frac{1}{2} \sum_{i=1}^{n} (c_i \cdot z_i^2)
\]  \hspace{1cm} (12)

Where:
- \(c_i\) – is the concentration of the \(i\)-th ion in the solution,
- \(z_i\) – is the charge of the \(i\)-th ion in the solution.

In the case of an electrolyte consisting of a mononegative anion and a monopositive cation (i.e. \(D^+A^-\)), the ionic strength is equal to the equilibrium concentration of the dissociated anion (or cation, as the concentrations of the anions and cations obtained via the dissociation of such an electrolyte are equal). Using the above, we can simplify Eq. 11b:

\[
\log(K) = \log(K^*) - 2 \cdot A \cdot \sqrt{\alpha \cdot C_0}
\]  \hspace{1cm} (13a)

Assuming that the measurement is conducted at the temperature of 25 degrees Celsius, the \(A\) constant for water is equal to 0.508 \(\text{mol}^{0.5} \cdot \text{kg}^{0.5}\). Linearising the above equation, we obtain the following dependence:

\[
\log(K^*) = \log(K) + 1.016 \cdot \sqrt{\alpha \cdot C_0}
\]  \hspace{1cm} (13b)

Based on the plot of \(\log K^*\) versus the square root of the product of the dissociation degree and the analytical concentration of the electrolyte, the value of the thermodynamic dissociation constant \((K)\) can be obtained by extrapolation to zero, either graphically or algebraically.
2. Conductometric measurements

The electrical conductivity of an electrolyte solution is calculated, based on the experimentally measured resistance of this solution and the conductometric vessel constant, according to the equation:

\[ \kappa = \frac{k_{\text{vessel}}}{R} \]  \hspace{1cm} (14)

Where:
- \( \kappa \) – is the electrical conductivity of the electrolyte solution [S·m\(^{-1}\)]
- \( k_{\text{vessel}} \) – is the conductometric vessel constant [m\(^{-1}\)],
- \( R \) – is the measured electrical resistance of the electrolyte solution [\( \Omega \)].

The molar conductivity of an electrolyte solution is calculated, using the following equation:

\[ \Lambda_m = \frac{k_p - k_w}{C_0} \]  \hspace{1cm} (15)

Where:
- \( \Lambda_m \) – is the molar conductivity of the electrolyte solution [m\(^2\)·S·mol\(^{-1}\)]
- \( k_w \) – is the electrical conductivity of deionised water [S·m\(^{-1}\)]
- \( k_p \) – is the electrical conductivity of the electrolyte solution [S·m\(^{-1}\)]
- \( C_0 \) – is the analytical molar concentration of the electrolyte [mol·m\(^{-3}\)]

Having knowledge about the boundary equivalent concentration of the investigated electrolyte and combining the above equation with Eq. 8 and Eq. 14, it is possible to use the resistances, measured for a series of electrolyte solutions, to determine the value of the classic dissociation pseudo-constant of the investigated weak acid and, afterwards, to determine the value of the thermodynamic dissociation constant, using Eq. 13b and extrapolating to \( C_0 = 0 \).
3. Potentiometric measurements

A fast and simple method for determining the estimate value of the dissociation constant of a weak acid uses the measurement of the pH of a solution containing the weak acid and its salt with a strong base.

The basis of this method is the Henderson – Hasselbach equation, known from the theory of ionic equilibria in electrolyte solutions:

\[
\text{pH} = \text{pK} + \log\left(\frac{C_{\text{SOLI}}}{C_{\text{KWASU}}}\right)
\]  

(16)

This method can be used to produce accurate approximations, when several conditions are met:

- The investigated acid should be a weak acid, so that the measured pH of the solution is between 4 and 10.
- The solution should contain equivalent amounts of the weak acid and its salt with a strong base, diluted sufficiently, so that the ionic strength of the solution does not affect the activities of the ions to any relevant degree.

If the equilibrium concentrations of the weak acid and its sodium salt are equal, Eq. 16 states that the measured pH of the solution will be numerically equal to the pK of the weak acid.

III. Experimental procedure

1. Conductometric method

Apparatus:
- Universal E-316 bridge and conductometric sensor,
- Ultra-thermostat,
- Thermostatic conductometric vessel,
Chemicals:

- Potassium chloride,
- Deionised and distilled water,
- Weak acid, as given by the exercise supervisor.

Procedure:

The manual for the electric bridge used for conductometric measurements is placed above the experimental setup – the financial responsibility for damage resulting from improper operation of the bridge and electrodes is hereby placed on the persons performing the exercise.

a) Turn the thermostat on and set temperature at 298 K.

b) Rinse the conductometric sensor and the thermostatic vessel three times with distilled water and afterwards once with deionised water.

   The conductometric sensor is a very fragile device and, therefore, one should exercise extreme caution when handling or operating it.

c) Fill the conductometric vessel with deionised water and submerge the conductometric sensor.

   When filling the conductometric vessel with deionised water, it should be ensured that the sensing element of the conductometric sensor is completely submerged, as well as that no air bubbles are present nearby the sensor.

d) After the set temperature stabilises, measure the resistance of the deionised water and determine its electrical conductivity.

   Conductivity measurements are performed always while the stirrer is turned off, after calming of the solution.

   The electrical conductivity of deionised water should be two orders of magnitude lower than determined later conductivities of acid solutions – one can then assume that it is within the limits of measurement error. Otherwise the conductivity of the water should be subtracted from conductivities of acid solutions.

   If the resistance of the deionised water is lesser than 50 [kΩ], repeat the rinsing procedure.
   If the measured value remains at a constant level, despite repeated rinsing, notify the supervisor and continue performing the exercise.

e) To a 100 ml volumetric flask pour 0.1 M aqueous solution (first-stage solution) of the weak acid, as given by the exercise supervisor.
f) By diluting the 0.1 M solution, in 50 ml volumetric flasks prepare a series of solutions with a gradually diminishing concentration, for example: 0.05; 0.025; 0.0125; 0.006; 0.005; 0.003 M and measure their resistance.

*Determination of the electrical conductivity of each of the prepared solutions should be performed starting from the most dilute one and finishing with the most concentrated, first-stage solution.*

*Every time prior to filling the cell with a solution for resistance measurement, rinse both the vessel and a probe with distilled water and then with a small amount of solution.*


\[ \text{g) Prepare 1 mM KCl solution by diluting 0.1 M KCl solution and measure its resistance in order to determine the cell constant. Electrical conductivity of 1 mM KCl solution at 298 K is } 0.014695 \text{ S·m}^{-1}. \]

2. **Potentiometric method**

**Apparatus:**
- CPC-502 digital pH-meter,
- Universal electrode.

**Chemicals:**
- Sodium hydroxide,
- Deionised water,
- Weak acid, as given by the exercise supervisor.

**Procedure:**
- Rinse the universal electrode of the pH-meter three times with distilled water and afterwards once with deionised water. After rinsing, gently dry the electrode, using the filtration paper scraps for this purpose.
- Prepare 50 ml of an equimolar solution of the acid and its salt with NaOH (summary concentration of 0.05 mol/L) and measure its pH.

IV. **Results and error analysis**

Calculate and compare values and uncertainty of the weak acid dissociation constant determined from the conductivity and potentiometric measurements.
V. Safety rules and waste disposal

1. Classification:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>irritating substance (Xᵢ)</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>irritating substance (Xᵢ)</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>corrosive substance (Xᵢ)</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>harmful substance (Xₚ)</td>
</tr>
<tr>
<td>p-Aminobenzoic acid</td>
<td>irritating substance (Xᵢ)</td>
</tr>
</tbody>
</table>

2. Dangers:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Dangers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>R:8, wywołuje oparzenia, poważne podrażnienie dróg oddechowych, kaszel, duszność, Ryzyko uszkodzenia rogówki i utraty wzroku;</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>R:8-36/37/38, drażni oczy i skórę, podrażnienie błon śluzowych jamy ustnej, gardła i przędy;</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>R:34, wywołuje oparzenia, podrażnienie błon śluzowych, kaszel, duszność, biegunka, wymioty;</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>R:8-22-36/37/38, działa szkodliwie w przypadku spożycia, działa drażniaco na oczy, podrażnienie dróg oddechowych;</td>
</tr>
<tr>
<td>p-Aminobenzoic acid</td>
<td>R:42/43, działa drażniaco na oczy, objawy podrażnienia dróg oddechowych;</td>
</tr>
</tbody>
</table>

3. Safety measures:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Measures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>S:17, szczelne opakowania, dobrze wentylowane pomieszczenie;</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>S:15-17-26-36, szczelne opakowania, suche dobrze wentylowane pomieszczenie;</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>S:15-16-26-36, szczelne opakowania, chłodne pomieszczenie;</td>
</tr>
</tbody>
</table>
Benzoic acid – S:22-36/37, szczelne opakowania, suche pomieszczenie;
p-Aminobenzoic acid – S:26-36, szczelne opakowania, suche pomieszczenie;

4. Waste disposal:

Strongly diluted aqueous solutions of the acids used in the exercise are to be disposed of via the sewer system.

WARNING: In the case of exposure to any of the dangerous substances, immediately notify the supervisor of the exercise.

VI. Control questions

1. Define the electrical conductivity of an electrolyte solution.
2. Define the molar conductivity and the limiting molar conductivity of an electrolyte solution.
3. What is the conductometric vessel constant and why do we need to determine it?
4. Describe the mechanism of charge transfer in electrolytes.
5. What determines the conductivity of the electrolyte?
6. Derive the formula for the dissociation constant electrolyte type $H_2A$ when $C_0$ and $\alpha$ are given.
7. Describe and discuss the structure and operation of an universal electrode for pH measurements of solutions.

VII. Literature


Last modification: 28.03.2019