Determining concentration by using mathematical method

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Abstract: Data analysis is an essential tenet of analytical chemistry, extending the possible of obtaining information from the measurement of chemical phenomena. Conductivity methods have grown considerably over recent years but their wide use is hindered because some still consider them too complicated. The purpose of this article is to describe a conductivity sensitivity method more simply from the point of view of an analytical chemist, by using mathematical linear and quadratic extrapolations. This conductivity sensitivity method defines sensitivity parameters for determining reactant or product concentrations based on measuring strong and weak electrolytes conductivities. The sensitivity parameters are constant throughout this specific reaction. Concentrations of strong electrolytes can be determined by linear extrapolation, whilst concentrations of weak electrolytes can be determined by quadratic mathematical extrapolation. This method proposes a continuous determination of real reactant or product concentrations.

Key words: conductivity sensitivity method, strong electrolyte, weak electrolyte, concentration.

1 Introduction

Determining concentrations is basic for analytical chemistry, using different methods. Eldridge and Piret [1] obtained the pseudo-first-order reaction rate constant using a batch reactor. In order to determine the acetic anhydride concentration, samples from the reactor were withdrawn into tarred flasks containing 15-20 times the quantity of saturated aniline-water required to react with the sample. Since the anhydride rapidly acetylates the aniline, thus producing acetanilide and acetic acid, the samples were then titrated to determine the concentration of acetic acid. In another study, Shatyski and Hanesian [2] determined the kinetics of the above reaction by using temperature-time data obtained under adiabatic conditions in a batch reactor. The use of in-situ FTIR spectroscopy has already been demonstrated, when following the hydrolysis of acetic anhydride reaction [3]. An analysis of the batch reactor's data showed that the hydrolysis of acetic anhydride is a pseudo-first order reaction. The rate constants were calculated from the batch data using both integral and differential methods of analysis.

Advances in electronics and computing over the past 30 years have revolutionized the analytical laboratory. Technological developments have allowed instruments to become smaller, faster, and cheaper, while continuing to increase accuracy, precision, and availability. Furthermore, software sold with many commercial instruments contains automatic data-processing algorithms. Advances in computing have allowed researchers to obtain increasing amounts of chemically-relevant information from their data; however, this is not always achieved using simple data-processing techniques. It is important to establish true mathematical models for utilization within the chemical industry [4, 5, 6, 7].

This paper studies the determining of reactant or product concentration by the determination of sensitivity parameters, using the conductivity sensitivity method.

2. The conductivity sensitivity method

The conductivity sensitivity method is an alternative method for accurately quantifying reactant or product concentrations. This method applies sensitivity parameters for determining concentrations for strong and weak electrolytes, by using conductivity. Specific characteristics can be found from the measurements, especially for strong and weak electrolytes. Concentrations of strong electrolytes can be determined by linear extrapolation, whilst concentrations of weak electrolytes can be determined by quadratic mathematical extrapolation. This method proposes a continuous determination of reactant or product concentrations.

Each reaction has specific characteristic sensitivity parameters which can be determined by using mathematical extrapolation. Conductivity for a specific reaction has a specific characterization, therefore certain sensitivity parameters can be determined – the sensitivity constant of conductivity, which is constant during the specific reaction.

This conductivity sensitivity method is a very simple method over two stages, individually, for both strong and weak electrolytes (Fig. 1):

Determining the concentration by using the theory of strong and weak electrolytes

Determining the sensitivity constant for strong and weak electrolytes

Firstly, some measurement of conductivity which depend on time are needed, especially for the strong (chapter 2.1.1) and weak electrolytes (chapter 2.2.1). According to this theory the strength or weakness of an electrolyte determines the concentrations of the reactant or product. Secondly, this data is sufficient to allow the sensitivity parameters - sensitivity constant of conductivity for strong (chapter 2.1.2), and weak electrolytes (chapter 2.2.2). The method is carried out separately for strong and weak electrolytes. It was tested for various real reactions (chapters 4. and 5.).

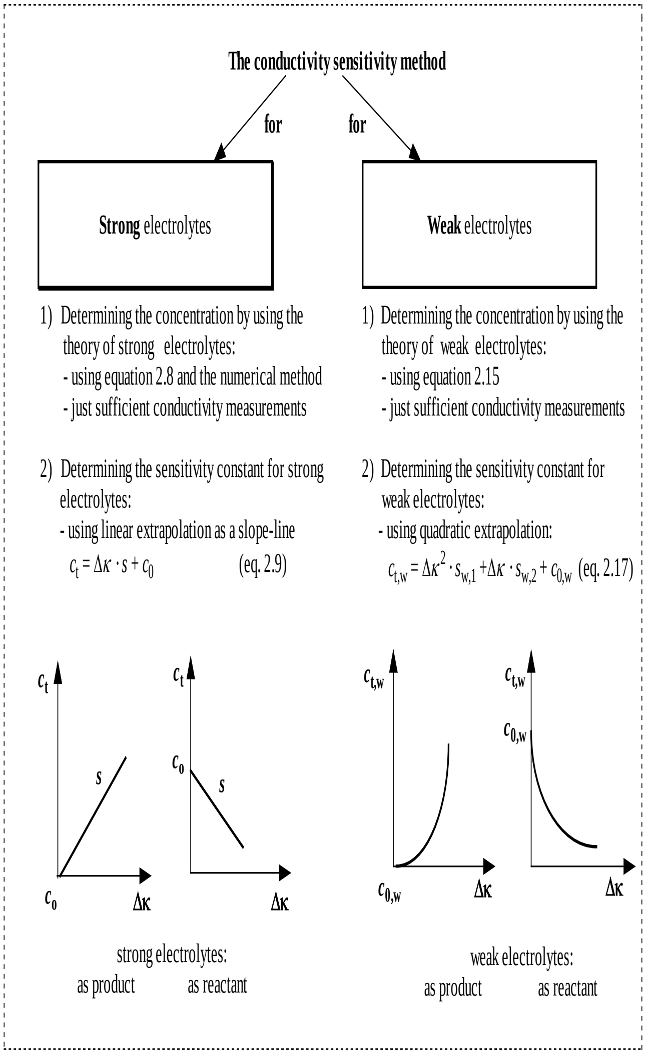

Figure 1:The Conductivity Sensitivity Method

2.1 The conductivity sensitivity method for strong electrolytes

2.1.1 Determining the concentration by using the theory of strong electrolytes

Strong electrolytes are substances that are almost fully ionized in solution, and include ionic solids and strong acids. As a result of their complete ionization, the concentration of ions in a solution is proportional to the concentration of the added strong electrolyte [8].

In an extensive series of measurements during the nineteenth century, Friedrich Kohlrausch showed that, at low concentrations, the molar conductivities of strong electrolytes vary linearly with the square root of the concentration:

$$\Lambda_m = \Lambda_m^o - K\sqrt{c} \qquad (2.1)$$

where Λ_m introduces the molar conductivity in siemens metre-squared per mole (S m^2 mol^{-1}), which is defined as:

$$\Lambda_m = \frac{\kappa}{c} \tag{2.2}$$

where c is the molar concentration of the added electrolyte, and κ is the conductivity in siemens per metre (S m^{-1}).
Equation 2.1 is called Kohlrausch's Law. The constant Λ_m^o is the limiting molar conductivity, the molar conductivity within the limit of zero concentration. The Λ_m^o for sodium hydroxide at a temperature of around 25°C is [8]:

$$\Lambda_m^o = 5.01 + 19.91 = 24.92 \text{ mS m}^2\text{ mol}^{-1} = 2492 \text{ mS dm}^2\text{ mol}^{-1} \tag{2.3}$$

Kohlrausch's constant can be calculated by known values for initial concentration (c_0) and initial conductivity (κ_0), using equation 2.1 and 2.2:

$$K = \frac{\Lambda_m^o}{c_0^{0.5}} - \frac{\kappa_0}{c_0^{1.5}} \tag{2.4}$$

The essence of the strong electrolytes theory is that you can determine the concentration of reactant or product. The reaction was observed by the concentration calculation. The two basic equations 2.1 and 2.2 were used:

$$\Lambda_m^o - K\sqrt{c} = \frac{\kappa}{c} \tag{2.5}$$

The concentration was expressed as a cubic equation:

$$c^3 - \frac{\Lambda_m^{o\,2} c^2}{K^2} + \frac{\Lambda_m^o 2\kappa c}{K^2} - \frac{\kappa^2}{K^2} = 0 \tag{2.6}$$

or in general:

$$ax^3 + bx^2 + cx + d = 0 \tag{2.7}$$

The concentration was expressed for equation 2.5 for the numerical method:

$$c = \frac{\kappa + c^{1.5}K}{\Lambda_m^o} \tag{2.8}$$

The concentration was calculated by using a numerical method (for example successive substitution; addition A). The initial concentration (*zc*) and the allowed differences between the initial and target values (*EPS*) are needed.

The determination of concentration change by using a numerical method is very long-term, so it is only used at the beginning so that you can determine the sensitivity constant of the conductivity (chapter 2.1.2). Further determination of concentration change by using sensitivity is faster and sufficiently precise.

2.1.2 Determining the sensitivity constant for strong electrolytes

The most important sensitivity parameters - sensitivity constant of conductivity (s) can be determined graphically by using linear extrapolation as a sloped-line for strong electrolytes, or using the equations (2.9 - 2.12):

$$c_t = \Delta\kappa \cdot s + c_0 \tag{2.9}$$

$$\Delta\kappa = \kappa_0 - \kappa_t \tag{2.10}$$

$$c_t = (\kappa_0 - \kappa_t)\cdot s + c_0 \tag{2.11}$$

$$s = (c_0 - c_t)/(\kappa_0 - \kappa_t) \tag{2.12}$$

The concentration dependence of time (c_t) can be calculated by using equations 2.9 or 2.11 with a difference in conductivity ($\Delta\kappa$; eq. 2.10). The sensitivity constant (s) can be calculated by using equation 2.12 or with sloped-lines (Fig. 1). c_0 is the known initial concentration and κ_0 is the known initial conductivity.

2.2 The conductivity sensitivity method for weak electrolytes

2.2.1 Determining the concentration by using the theory of weak electrolytes

Weak electrolytes are not fully ionised in solution [8]. They include weak Bronsted acids and bases, such as CH_3COOH and NH_3. The marked concentration dependence of their molar conductivities arises from displacement of the equilibrium:

$$HA(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{a_{H3O+} \cdot a_{A-}}{a_{HA}}$$

towards products at low molar concentrations.
The conductivity depends on the number of ions in the solution and, therefore, on the degree of ionisation, α, of the electrolyte; when referring to weak acids, we speak of the degree of

deprotonation. It is defined so that, for the acid HA at a molar concentration c, at equilibrium:
$[H_3O^+] = \alpha c \quad [A^-] = \alpha c \quad [HA] = (1-\alpha)c$
If we ignore the activity coefficients, the acidity constant, K_a, is approximately:

$$K_a = \frac{\alpha^2 \cdot c}{1-\alpha} \tag{2.13}$$

The acid is fully deprotonated at infinite dilution, and its molar conductivity is then Λ_m^o. Because only a fraction α is actually present as ions in the actual solution, the measured molar conductivity Λ_m is given by:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^o} \tag{2.14}$$

For the weak electrolyte, the α is almost 0, and for the strong electrolyte the α draws nearer to 1.
The concentration, c, is calculated from the eq. 2.13:

$$c = \frac{K_a \cdot (1-\alpha)}{\alpha^2} \tag{2.15}$$

The prior of the concentration for determining the degree of ionisation, α, which is calculated from the eq. 2.14 by considering eqs. 2.2 and 2.15:

$$\alpha = \frac{\Lambda_m^o \cdot K_a}{(\kappa + \Lambda_m^o \cdot K_a)} \tag{2.16}$$

2.2.2 Determining the sensitivity constant for weak electrolytes

The sensitivity parameters - sensitivity constants of conductivity ($s_{w,1}, s_{w,2}$) can be determined graphically by using quadratic mathematical extrapolation for weak electrolyte, or using the equations (2.17 - 2.19):

$$c_{t,w} = \Delta\ \kappa^2 \cdot s_{w,1} + \Delta\ \kappa \cdot s_{w,2} + c_{0,w} \tag{2.17}$$

$$\Delta\kappa_w = \kappa_{0,w} - \kappa_{t,w} \tag{2.18}$$

$$c_{t,w} = (\kappa_{0,w} - \kappa_{t,w})^2 \cdot s_{w,1} + (\kappa_{0,w} - \kappa_{t,w}) \cdot s_{w,2} + c_{0,w} \tag{2.19}$$

The concentration dependence of time ($c_{t,w}$) can be calculated by using equations 2.17 or 2.19 with the difference in conductivity ($\Delta\kappa$; eq. 2.18). The sensitivity constants ($s_{w,1}$, $s_{w,2}$) are constants of a quadratic equation (2.17). $c_{0,w}$ is the known initial concentration and $\kappa_{0,w}$ is the known initial conductivity.

3. Case study for strong electrolytes

The conductivity sensitivity method was tested to synthesize methoxide and sodium benzoate. Sodium hydroxide (NaOH), is in both cases, the reactant and a strong electrolyte.

3.1 Methoxide synthesis

Methoxide (CH_3O^-) was produced from sodium hydroxide (NaOH) and methanol (MeOH) in a batch reactor:

$$\underset{A}{NaOH} + \underset{B}{CH_3OH} = H_2O + Na^+ + \underset{C}{CH_3O^-} \tag{R1}$$

The main application of sodium methoxide (CH_3ONa) today is its use as a catalyst in the production of bio-diesel. During this process, vegetable oils or animal fats, which are chemically fatty acid triglycerides, are transesterified with methanol to produce fatty acid methyl esters (FAMEs).

3.1.1 Determining the concentration by using the theory of strong electrolytes

A schematic diagram of the laboratory apparatus is shown in Figure 2. A batch reactor with a stirrer was used in the experiment. Methanol (0.12 mL) was heated into a reactor at a temperature of 28 °C, and 3.34 g pure NaOH was dissolved in 500 mL of water. Both substances were mixed and the conductivity (κ_t) depending on time, t (Table 1) was measured. First the conductivity of the sodium hydroxide (κ_0) was 247 mS/dm. The initial sodium hydroxide concentration, c_{A0}, was 0.167 mol/L. The molar conductivity at infinite dilution (Λ_m^o) of the sodium hydroxide was 2492 mS dm^2 mol^{-1} [8] at a temperature around 25°C (eq. 2.3). Kohlrausch's constant can be calculated by known values of the initial concentration (c_{A0}) and the initial conductivity (κ_0), using equation 2.4, and was 2478.74 mS dm^2/((mol L^{-1})$^{1/2}$ mol).

The concentration was calculated by using equation 2.8 and a numerical method (for example successive substitution; addition A). The initial concentration (zc) and the allowed difference between the initial and target values (EPS) are needed (Table 1). Figure 3 illustrates the plot of sodium hydroxide concentration, c_A, as a function of time at a temperature of 28ºC.

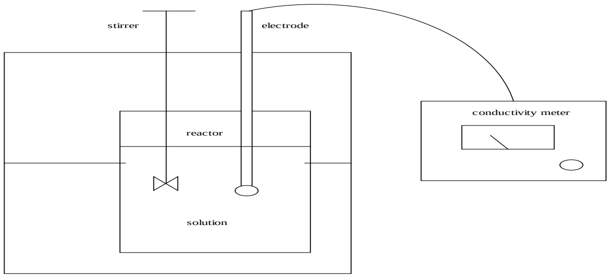

Figure 2: The apparatus – stirred batch reactor

Table 1: Experimental data and calculation for methoxide synthesis, using conductivity.

t/min	κ/(mS/dm)	c_A /(mol/L)	$\Delta\kappa$ /(mS/dm)
0.00	247.0	0.167000	0.0
0.80	240.0	0.159922	7.0
0.91	238.0	0.157882	9.0
1.25	236.7	0.156556	10.3
2.00	234.1	0.153904	12.9
2.25	233.5	0.153292	13.5
2.58	232.7	0.152476	14.3
3.16	231.4	0.151150	15.6
3.83	230.3	0.150028	16.7
4.33	229.5	0.149212	17.5
4.83	228.8	0.148498	18.2
5.58	227.8	0.147478	19.2
6.00	227.3	0.146968	19.7
7.00	226.2	0.145846	20.8
8.00	225.6	0.145234	21.4

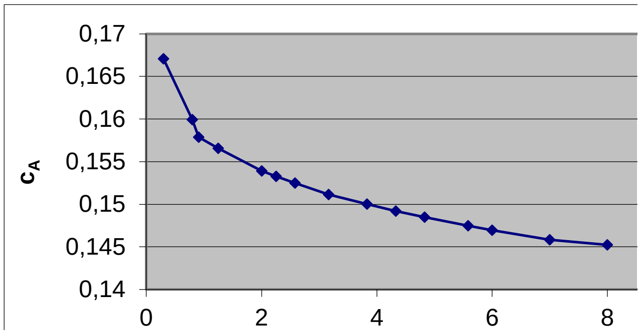

Figure 3: Concentration of sodium hydroxide, c_A, as a function of time at 28ºC.

Calculating the concentration was also checked using titration. The same experiment was carried out at 28 ºC by analysing a concentration, using titration. (Table 2). 20 mL 0.1 mol/L HCl was added to the 10 mL sample which stopped the reaction, and retitration with 0.1 mol/L NaOH took place:

$$mol_{HCl} = mol_{NaOH} + mol_{sample}$$

$$20 \cdot 0.1 = 0.1 \cdot V_{NaOH} + 10 \cdot c_A \qquad (3.1)$$

Table 2: Experimental data and calculation for methoxide synthesis, using titration.

t/min	V_{NaOH} /mL	c_A/(mol/L)
2.66	5.5	0.145
4.00	5.6	0.144
6.58	5.7	0.143
7.00	5.8	0.142
9.00	5.9	0.141

Titration confirmed the measurement accuracy using conductivity.

3.1.2 **Determining the sensitivity constant for strong electrolytes**

Concentration, c_t, as a dependent variable is shown on the y-axis. Difference in conductivity, $\Delta\kappa$ (eq. 3.2), as an independent variable is shown on the x-axis (Fig. 4; Table 1).

$$\Delta\kappa = \kappa_0 - \kappa_t = 247 - \kappa_t \qquad (3.2)$$

Now that we know the constant parameters of line - the sensitivity constant of conductivity (s), therefore, any value of reactant concentration can be calculated (eq. 3.3):

$$c_t = \Delta\kappa \cdot s + c_0 = c_t = \Delta\kappa \cdot \left| -0.001 \right| + 0.167 \qquad (3.3)$$

The slope is negative, because the reactant concentration (NaOH) is decreasing. Parameters are graphically defined along the ideal-fit line. The sensitivity constant of conductivity (s) is just the sloped-line with the absolute value 0.001. c_0 as the known initial concentration is 0.167.

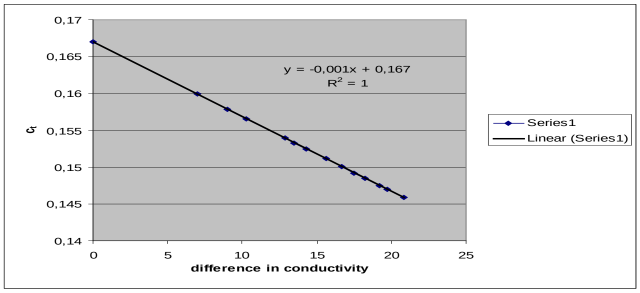

Figure 4: Linear extrapolation for methoxide synthesis.

3.2 Sodium benzoate synthesis

Sodium benzoate ($NaC_6H_5CO_2$) is a preservative. It is bacteriostatic and fungistatic under acidic conditions. Sodium benzoate is indicated on a product label as E211. Sodium benzoate is produced by the neutralization of benzoic acid ($C_7H_6O_2$) with sodium hydroxide (NaOH):

$$\underset{A}{NaOH} + \underset{B}{C_7H_6O_2} \leftrightarrow \underset{C}{NaC_6H_5CO_2} + \underset{D}{H_2O} \quad (R2)$$

3.2.1 Determining the concentration by using the theory of strong electrolytes

A schematic diagram of the laboratory apparatus is shown in Figure 2. A batch reactor with a stirrer was used in the experiment. Sodium hydroxide (0.28546 g) was dissolved in water (0.1 L) and heated in a reactor at a temperature of 19 °C. 0.88 g benzoic acid dissolved in 0.5 L of water was added.

Both substances were mixed and the conductivity (κ_t) depending on time, *t* (Table 3) was measured.

First the conductivity of the sodium hydroxide (κ_0) was 28.0 mS/dm.

The initial sodium hydroxide concentration, c_{A0}, was 0.01185 mol/L. The molar conductivity at infinite dilution (Λ_m^o) of the sodium hydroxide was 2492 mS dm^2 mol^{-1} [8] at a temperature of around 25°C (eq. 2.3). Kohlrausch's constant can be calculated by known values of initial concentration (c_{A0}) and initial conductivity (κ_0), using equation 2.4 and was 1186.23 mS $dm^2/((mol\ L^{-1})^{1/2}\ mol)$. Further concentration was calculated by using the numerical method (eq. 2.8; Table 4).

Figure 5 illustrates the plot of sodium hydroxide concentration, c_A, as a function of time at a temperature of 19 ºC.

Table 3: The experimental data and calculation for sodium benzoate synthesis, using conductivity.

t/min	κ_t /(mS/dm)	c_A /(mol/L)
0.00	28.00	0.011850
0.61	2.497	0.001073
1.00	2.486	0.001068
1.41	2.477	0.001064
1.73	2.468	0.001060
2.23	2.452	0.001053
2.93	2.433	0.001044
3.78	2.414	0.001036
4.20	2.405	0.001032
5.00	2.390	0.001025
6.03	2.376	0.001019
7.05	2.362	0.001012
8.48	2.348	0.001006
9.80	2.338	0.001002
11.78	2.329	0.001001
13.66	2.322	0.001000
15.18	2.317	0.001000
17.48	2.313	0.001000
20.00	2.313	0.001000

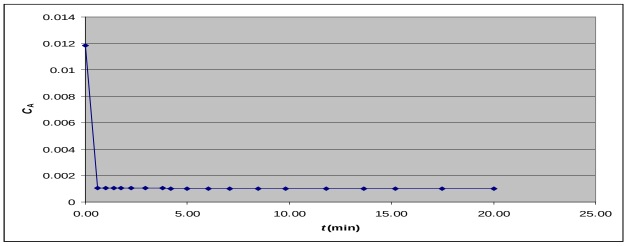

Figure 5: Concentration of sodium hydroxide, c_A, as a function of time at 19 ºC.

Table 4: Concentration data as giving by the numerical method.

t/min	c_A /(mol/L)
0.7	0.00108627
0.86	0.00108615
1.30	0.00108567

3.2.2 Determining the sensitivity constant for strong electrolytes

Concentration, c_t, as a dependent variable is shown on the y-axis. Difference in conductivity,

$\Delta\kappa$ (eq. 3.4), as an independent variable is shown on the x-axis (Fig. 6; Table 3).

$$\Delta\kappa = \kappa_0 - \kappa_t = 28 - \kappa_t \qquad (3.4)$$

Now that we know the constant parameters of the line - the sensitivity constant of conductivity (s), therefore, can be calculate any value of reactant concentration (eq. 3.5):

$$c_t = \Delta\kappa \cdot s + c_0 \quad = c_t = \Delta\kappa \cdot \left|-0.0004\right| + 0.0119 \qquad (3.5)$$

The slope is negative, because reactant concentration (NaOH) is decreasing. Parameters are graphically defined, and the ideal fit-line. The sensitivity constant of conductivity (s) is just the sloped-line with the absolute value 0.0004. c_0 as the known initial concentration is 0.01185.

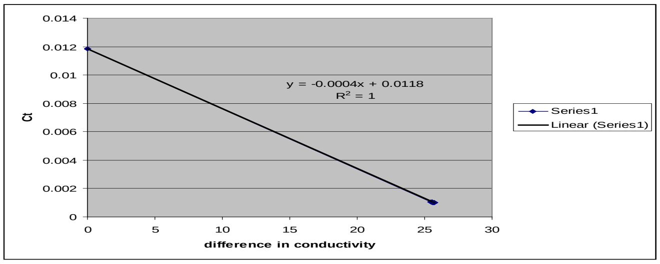

Figure 6: Linear extrapolation for sodium benzoate synthesis.

4. Case study for weak electrolytes

The conductivity sensitivity method was tested to synthesize aspirin and acetic acid. Acetic acid (CH_3COOH) is, in both cases, the product or by-product and a weak electrolyte.

4.1 Aspirin synthesis

Aspirin, also known as acetyl-salicylic acid ($H_3CCOOC_6H_4COOH$) is a salicylate drug, often used as an analgesic to relieve minor aches and pains, as an antipyretic to reduce fever, and as an anti-inflammatory medication.

Aspirin synthesis is synthesized from salicylic acid (HOC_6H_4COOH) and acetic anhydride ($(CH_3CO)_2O$):

HOC_6H_4COOH + $(CH_3CO)_2O$ ↔
$H_3CCOOC_6H_4COOH$ + CH_3COOH (R3)
A B D
C

4.1.1 **Determining the concentration by using the theory of weak electrolytes**

A batch reactor with a stirrer was used in the experiment (Fig. 2). Salicylic acid (0.72 g) was dissolved in water (0.5 L) and heated in a reactor at a temperature of 25 °C. 50 % surplus of acetic anhydride was added.

First the conductivity of the poor salicylic acid (κ_0) was measured before reaction R1 took place. Acetic acid was produced as a by-product by aspirin synthesis. The conductivity of acetic acid was as κ_t.

Both substances were mixed and the conductivity (κ_t) depending on time, t (Table 5) was measured. The initial salicylic acid concentration, c_{A0}, was 0.0104 mol/L. The initial acetic acid concentration, c_{C0}, was 0.0 mol/L. The molar conductivity at infinite dilution (Λ_m^o) of the acetic acid was 39.05 mS m^2 mol^{-1} [8] at a temperature of around 25°C. The dissociation constant, K_a was 0.0000175 at a temperature of around 25°C. After conductivity measurements, the following could be calculated:

degree of ionization, α, from eq. 2.16
concentration of acetic acid, c_c, from eq. 2.15 (Table 5).

The reacted acetic anhydride, $c_{A(reacted)}$, could be calculated (Table 5) by using equation (4.1):

$$c_{A(reacted)} = c_c \qquad (4.1)$$

The non-reacted acetic anhydride is:

$$c_{A(non\text{-}reacted)} = c_A = c_{A0} - c_{A(reacted)} \qquad (4.2)$$

Figure 7 illustrates the plot of salicylic acid concentration, c_A, as a function of time at a temperature of 25ºC.

Table 5: The experimental data and calculation for aspirin synthesis.

t/min	κ_t/(mS/m)	c_c /(mol/L)	c_A /(mol/L)
0.00	1.236	0.000000000	0.010400
0.48	1.252	0.000136904	0.010263
0.57	1.258	0.000237708	0.010162
0.75	1.263	0.000342321	0.010058
0.92	1.266	0.000414083	0.009986
1.03	1.268	0.000465671	0.009934
1.13	1.270	0.000520257	0.009880
1.25	1.272	0.000577841	0.009822

1.37	1.273	0.000607757	0.009792
1.50	1.275	0.000669838	0.009730
1.58	1.277	0.000734917	0.009665
1.70	1.279	0.000802993	0.009597
1.82	1.280	0.000838156	0.009562
2.03	1.283	0.000948140	0.009452
2.15	1.285	0.001025210	0.009375
2.32	1.287	0.001105278	0.009295
2.50	1.289	0.001188343	0.009212
2.65	1.291	0.001274407	0.009126
2.88	1.294	0.001409123	0.008991
3.28	1.298	0.001599238	0.008801
3.42	1.300	0.001698792	0.008701
3.87	1.304	0.001906893	0.008493
3.97	1.306	0.002015440	0.008385
4.22	1.308	0.002126986	0.008273
4.57	1.311	0.002299925	0.008100
4.73	1.313	0.002418964	0.007981
5.00	1.315	0.002541002	0.007859
5.28	1.317	0.002666038	0.007734
5.50	1.319	0.002794071	0.007606
5.67	1.320	0.002859212	0.007541
6.07	1.323	0.003059132	0.007341
6.35	1.325	0.003196159	0.007204
6.50	1.326	0.003265797	0.007134
6.75	1.328	0.003407320	0.006993
7.15	1.330	0.003551842	0.006848
7.50	1.332	0.003699362	0.006701
7.67	1.333	0.003774246	0.006626
7.95	1.335	0.003926262	0.006474
8.12	1.336	0.004003394	0.006397
8.50	1.338	0.004159907	0.006240
8.80	1.339	0.004239288	0.006161
9.37	1.342	0.004481927	0.005918

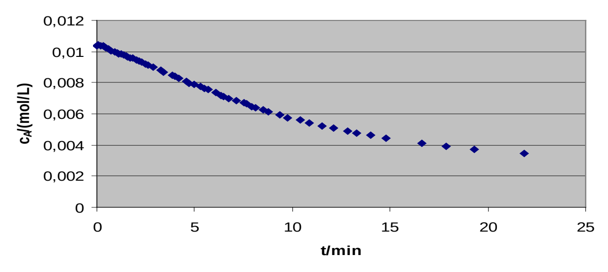

Figure 7: Concentration of salicylic acid, c_{A}, as a function of time at 25ºC.

4.1.2 **Determining the sensitivity constant for weak electrolytes**

Concentration, $c_{t,w}$, as a dependent variable, is shown on the y-axis. Difference in conductivity, $\Delta\kappa$ (eq. 4.3), as an independent variable, is shown on the x-axis (Fig. 8). Acetic acid as weak electrolyte is by-product, therefore, the conductivity was increasing.

$$\Delta\kappa = \kappa_t - \kappa_0 = \kappa_t - 1.236 \qquad (4.3)$$

The sensitivity parameters - sensitivity constants of conductivity ($s_{\mathrm{w},1}$, $s_{\mathrm{w},2}$) were determined graphically by using quadratic mathematical extrapolation for weak electrolytes:

$$c_{t,\mathrm{w}} = \Delta\kappa^2 \cdot s_{\mathrm{w},1} + \Delta\kappa \cdot s_{\mathrm{w},2} + c_{0,\mathrm{w}} = \Delta\kappa^2 \cdot 0.3747 + \Delta\kappa \cdot 0.0026 + 0.0 \qquad (4.4)$$

The sensitivity constants of conductivity ($s_{\mathrm{w},1}$, $s_{\mathrm{w},2}$) are 0.3747 and 0.0026. $c_{0,\mathrm{w}}$ as the known initial concentration is 0.0. Now that we know the sensitivity constants of conductivity, therefore, any value for product concentration can be calculated.

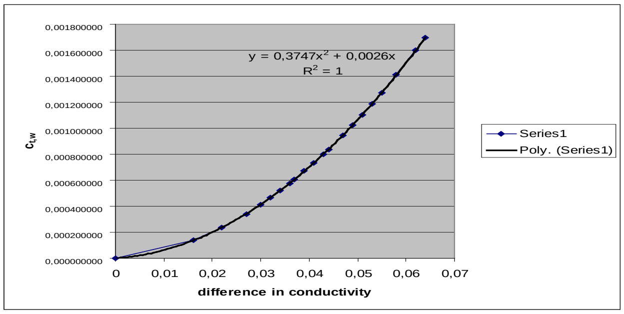

Figure 8: Quadratic extrapolation for aspirin synthesis.

4.2 Acetic acid synthesis

The hydrolysis of acetic anhydride to acetic acid was synthesized by measuring the conductivity. The measurements were based on the conductivity of a weak electrolyte. The reaction kinetics when producing acetic acid (CH_3COOH) from acetic anhydride ($(CH_3CO)_2O$) and water (H_2O):

$$(CH_3CO)_2O + H_2O = 2\ CH_3COOH \qquad (R4)$$

A B C

4.2.1 **Determining the concentration by using the theory of weak electrolytes**

A schematic diagram of the laboratory apparatus is shown in Figure 2. Reactor with a stirrer was used in the experiment. Distilled water (1L) is heated in a reactor at a temperature of 23 °C and 40 mL of acetic anhydride added at the same temperature. It then begins to measure the conductivity (κ) in dependence on time, *t* (Table 6). The molar ratio between acetic anhydride (Ac) and water (H_2O) is *f*(Ac:H_2O) = 1:131.

The initial acetic anhydride concentration, c_{A0}, is 0.4075 mol/L. The initial acetic acid concentration, c_{C0}, is 0.0 mol/L. The molar conductivity at infinite dilution (Λ_m^o) of acetic acid is 39.05 10^{-3} S m^2 mol^{-1} [8], the acidity constant, K_a, is 1.75 10^{-5} at a temperature around 25°C. It is assumed that the Λ_m^o and K_a are constant at a temperature of around 25 °C (± 5°C). Figure 9 illustrates the plot of c_A as a function of time at a temperature of 23ºC. After conductivity, the following measurements can be calculated:

- degree of ionization, *α,* from eq. 2.16
- concentration of acetic acid, *c*, from eq. 2.15 (Table 6).

The reactive acetic anhydride can be calculated (Table 6):

$$c_{\text{A(reacted)}} = \frac{c}{2} \qquad (4.5)$$

The non-reactive acetic anhydride is:

$$c_{\text{A(non-reacted)}} = c_{\text{A}} = c_{\text{A0}} - c_{\text{A(reacted)}} \qquad (4.6)$$

Table 6: The experimental data and calculation for acetic acid synthesis.

t/min	*κ*/(μS/cm)	*c*/(mol/L)	$c_{\text{A(reacted)}}$/ (mol/L)	c_A /(mol/L)
0.00	20.0	0.00000	0.00000	0.40750
1.15	431.7	0.07102	0.03551	0.37199
2.62	692.0	0.18142	0.09071	0.31679
4.05	873.6	0.28854	0.14427	0.26323
6.07	1051.1	0.41716	0.20858	0.19892
8.08	1163.2	0.51056	0.25528	0.15222
10.08	1244.4	0.58411	0.29205	0.11545
13.03	1323.0	0.66001	0.33001	0.07749
14.80	1354.0	0.69122	0.34561	0.06189
16.03	1370.0	0.70762	0.35381	0.05369
18.02	1391.0	0.72942	0.36471	0.04279
20.03	1406.0	0.74520	0.37260	0.03490
22.87	1420.0	0.76008	0.38004	0.02746
24.78	1427.0	0.76757	0.38379	0.02371
28.25	1435.0	0.77618	0.38809	0.01941
31.12	1438.0	0.77942	0.38971	0.01779
34.75	1442.0	0.78375	0.39188	0.01562

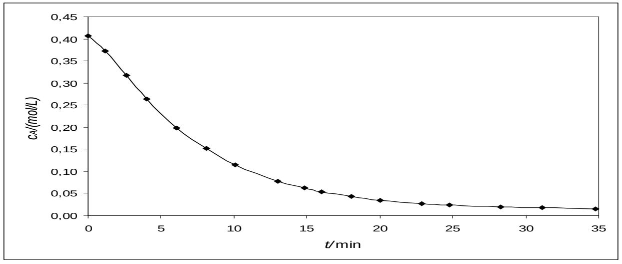

Figure 9: Concentration of acetic anhydride, c_A, as a function of time at 23ºC.

4.2.2 Determining the sensitivity constant for weak electrolytes

Concentration, $c_{t,w}$, as a dependent variable is shown on the y-axis. Difference in conductivity, $\Delta\kappa$ (eq. 4.7), as an independent variable is shown on the x-axis (Fig. 10). Acetic acid as a weak electrolyte is a product, therefore, the conductivity was increasing.

$$\Delta\kappa = \kappa_t - \kappa_0 = \kappa_t - 20.0 \qquad (4.7)$$

The sensitivity parameters - sensitivity constants of conductivity ($s_{w,1}$, $s_{w,2}$) were determined graphically by using quadratic mathematical extrapolation for weak electrolytes:

$$c_{t,w} = \Delta\kappa^2 \cdot s_{w,1} + \Delta\kappa \cdot s_{w,2} + c_{0,w} = \Delta\kappa^2 \cdot 0.0000004 + \Delta\kappa \cdot 0.00002 + 0.0 \qquad (4.8)$$

The sensitivity constants of conductivity ($s_{w,1}$, $s_{w,2}$) are 0.0000004 and 0.00002. $c_{0,w}$ as the known initial concentration is 0.0. Now that we know the sensitivity constants of conductivity, therefore, any value for product concentration can be calculated.

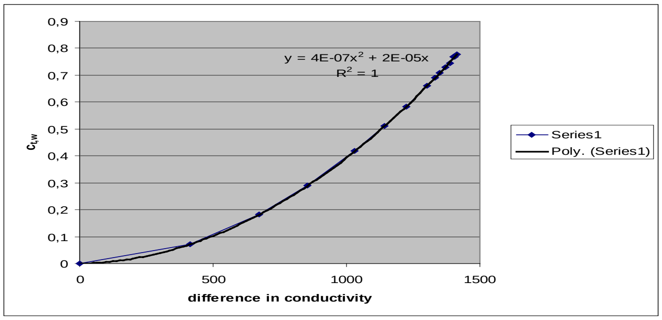

Figure 10: Quadratic extrapolation for acetic acid synthesis.

5. Conclusions

Determining concentration plays an important role in chemical engineering, so it could represent both continuous and static methods for concentration determination. The continuous method, by using conductivity, is very useful for uninterrupted concentration measurements.

The conductivity sensitivity method is an alternative method for accurately quantifying reactant or product concentrations. The conductivity sensitivity method is a very simple method over two stages, individually, for both strong and weak electrolytes:

1) Determining the concentration by using the theory of strong and weak electrolytes

2) Determining the sensitivity constant for strong and weak electrolytes.

This method applies sensitivity parameters for determining reactant or product concentrations for strong and weak electrolytes, by using conductivity. Specific characteristics can be found from the measurements, especially for strong and weak electrolytes. Concentrations of strong electrolytes can be determined by linear extrapolation, whilst concentrations of weak electrolytes can be determined by quadratic mathematical extrapolation. This method proposes a continuous determination of reactant or product concentrations.

Each reaction has specific characteristic sensitivity parameters which can be determined by using mathematical extrapolation. Conductivity for a specific reaction has a specific characterization, therefore, certain sensitivity parameters can be determined – the sensitivity constant of conductivity, which is constant during the specific reaction. Now that we know the sensitivity constants of conductivity, therefore, any value for reactant or product concentration can be calculated.

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Nomenclature

c	concentration, mol/L
K	constant in Kohlrausch equation, mS $m^2/((mol\ L^{-1})^{1/2}\ mol)$
k	reaction rate constant
n, m	rate order, /
r	rate of reaction
R	gas law constant, J/(mol · K)
T	temperature, K
t	time of reaction, min
X	degree of conversion, 1
κ	conductivity, mS/dm
Λ_m^o	molar conductivity at infinite dilution, S $m^2\ mol^{-1}$
Λ_m	molar conductivity, S $m^2\ mol^{-1}$