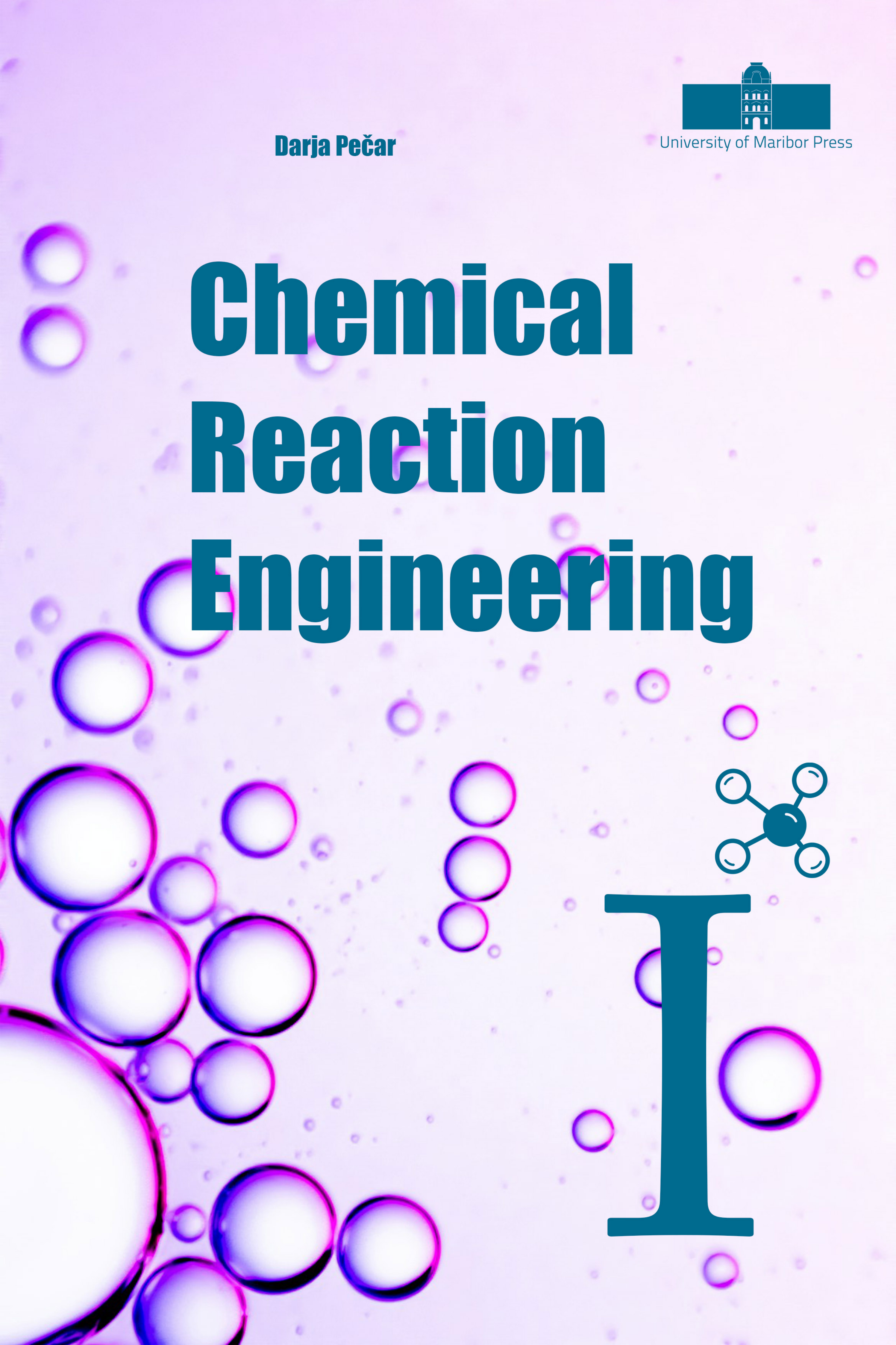

Darja Pečar

University of Maribor Press

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Chemical Reaction Engineering I

Manual for Performing Laboratory Exercises

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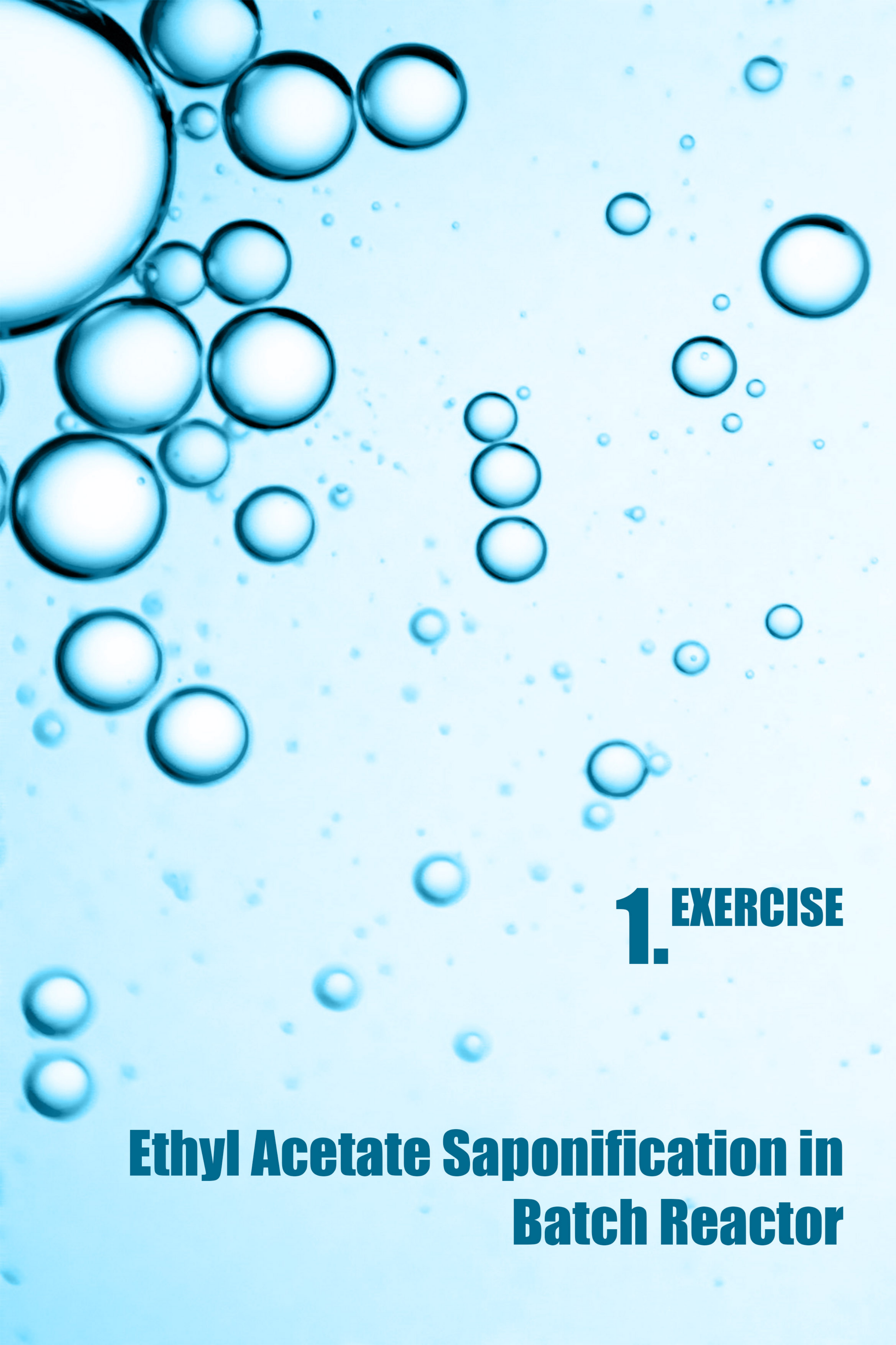


1. EXERCISE

Ethyl Acetate Saponification in Batch Reactor

Purpose of the exercise

The purpose of the exercise is to perform the saponification of ethyl acetate using sodium hydroxide in batch reactor. The reaction can be written as:

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

Theoretical background

The concentration of sodium hydroxide in the sample will be determined by re-titration and can be calculated using the following equation:

$$c_A = \frac{c_{NaOH}\,(V_{HCl} - V_{NaOH})}{V_{HCl}} \tag{1.1}$$

where: c_{NaOH} is the concentration of sodium hydroxide used for titration, V_{NaOH} volume of used sodium hydroxide, V_{HCl} volume of hydrochloric acid used to neutralize the sample.

The saponification of ethyl acetate with sodium hydroxide is an irreversible second order reaction. The equation for the reaction rate expressed with respect to the reactant A is writen as:

$$-r_A = -\frac{dc_A}{d\tau} = k\,c_A^2 \tag{1.2}$$

where: c_A sodium hydroxide concentration, t time and k reaction rate constant.

Integrating this equation, we get:

$$\frac{1}{c_A} - \frac{1}{c_{A0}} = k\,t \tag{1.3}$$

where: c_{A0} initial concentration of sodium hydroxide.

If we plot graph $1/c_A$ regarding t, we can determine the reaction rate constant from the slope of the line k.

The conversion of ethyl acetate is:

$$X_A = 1 - \frac{c_A}{c_{A0}} = \frac{c_C}{c_{A0}} \tag{1.7}$$

Activation energy

For the determination of the activation energy for selected reaction it is necessary that the reaction is carried out at least at three different temperatures. It is known that the temperature affects the reaction rate constant. Activation energy and pre-exponential factor are obtained from the Arrhenius equation:

$$k = k_0 \, e^{-\frac{E_a}{R\,T}} \tag{1.8}$$

where: k_0 is the pre-exponential factor, R gas constant, T temperature and E_a activation energy.

Accessories and chemicals

- beakers,
- measuring cylinders,
- measuring flasks,
- EtAc,
- NaOH,
- thermometers,
- thermostat,
- stirrer,
- conductivity meter,
- stopwatch,
- batch reactor.

Experimental procedure

The experiments will be carried out in a batch reactor. Prepare 3 L of sodium hydroxide solution with the concentration, $c_{A0} = 0.1$ mol·L^{-1} and 3 L of ethyl acetate solution with the concentration, $c_{B0} = 0.1$ mol·L^{-1}. Prepare Erlenmeyer flasks for retitration. Put 10 mL of hydrochloric acid with a concentration of $c = 0.1$ mol·L^{-1} and 2-3 drops of the phenolphthalein indicator into each Erlenmeyer flask. Fill the burette with a sodium hydroxide solution with a concentration of $c = 0.1\ \mathrm{mol \cdot L^{-1}}$.

The reactions will be conducted at temperatures T = (25, 30, 35 and 40) °C. Fill the batch reactor with 600 mL of ethyl acetate solution. Put a measuring cylinder with 600 mL of sodium hydroxide solution directly in the thermostat. Prior to the start of the reaction both solutions must be thermostated at least 10 min at the desired reaction temperature. Start the reaction by pouring the sodium hydroxide solution into the batch reactor containing the ethyl acetate solution, and simultaneously start the timer. At the same time, take the first sample (10 mL) and put it in the prepared Erlenmeyer flask. Record the time when the last drop of the sample falls into the Erlenmeyer flask. Then take samples at various time intervals, initially more often, the first five samples consecutively, then every 2 minutes. The unreacted sodium hydroxide in the sample will be neutralized by the hydrochloric acid, which results in termination of the reaction. The excess hydrochloric acid is then titrated with sodium hydroxide. Record time and consumption - volume during titration. The experiment is carried out for 30 minutes. Repeat the experimental procedure for all other temperatures.

Calculation and results

- for each temperature create a table with the t, c_A in $1/c_A$,
- plot c_A regarding time, t,
- plot $1/c_A$ regarding time, t,
- plot X_A regarding time, t at different temperatures, T,
- create a table with the reaction rate constants, k, and their logarithmic values, $\ln k$, at each temperature, T,
- plot Arrhenius plot,
- calculate pre-exponential factor, k_0, and activation energy, E_a.

2. EXERCISE

Determination of Residence Time in Continuous Flow Reactors

Purpose of the exercise

The purpose of the exercise is to determine the residence time distribution in continuous flow reactors.

Theoretical background

The residence time distribution is determined using the pulse injection method. The conductivity of the reaction fluid will be measured at the outlet of each continuous flow reactor over time. And because the concentration of the reaction fluid is proportional to the conductivity of the reaction fluid, thus we can write:

$$A = \int_0^\infty \kappa \, \mathrm{d}t \tag{2.1}$$

where: A is the area under the curve, κ the conductivity and t time. External residence time distribution (exit age distribution), $E(t)$, is then defined:

$$E(t) = \frac{\kappa(t)}{\int_0^\infty \kappa \, \mathrm{d}t} \tag{2.2}$$

The area under the curve $E(t) = \mathrm{f}(t)$ is equal to 1:

$$\int_0^\infty E(t) \, \mathrm{d}t = 1 \tag{2.3}$$

The mean residence time is determined from:

$$\bar{t} = \int_0^\infty t \, E(t) \, \mathrm{d}t \tag{2.4}$$

If there are no dead or stagnant zones within the reactor, then $\bar{t}$ is equal to τ:

$$\tau = \frac{V}{q} \tag{2.5}$$

where: V is the volume and q flow through the reactor.

Accessories and chemicals

- syringe,
- solution of $KNO_3 + KMnO_4$,
- conductivity meters,
- different continuous reactors.

Experimental procedure

Experiments will be conducted in plug flow, mixed flow and cascade mixed flow continuous reactors. The residence time distribution will be determined by pulse injection. Each reactor is equipped with an injection spot at the inlet of the reactor and a conductivity meter at the outlet of the reactor. Adjust the valves to the appropriate positions to allow deionized water to flow through the reactor at the desired flow rate. Maintain a constant flow through the reactor to ensure a consistent residence time. Prepare the syringe with a specified amount of the solution $KNO_3 + KMnO_4$. At the same time inject the solution in one portion into the reactor and start the measuring procedure in the program on a computer. Conductivity will be measured every 5 seconds. At the end of the experiment the value of the conductivity should be approximately the same as at the beginning of the experiment. Repeat the experimental procedure for all other continuous reactors.

Calculation and results

- plot κ regarding t for each reactor,
- plot $E(t)$ regarding t for each reactor,
- plot $t \cdot E(t)$ regarding t for each reactor,
- calculate the theoretical residence time,
- determine practical residence time,
- create a table with the theoretical and practical values of residence for all reactors.

3. EXERCISE

Ethyl Acetate Saponification in Continuous Reactors

Purpose of the exercise

The purpose of the exercise is to perform the saponification of ethyl acetate with sodium hydroxide in different continuous flow reactors. The reaction can be written as:

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

Theoretical background

Practical value of concentration

Using Kohlrausch's law, it is possible to determine the concentrations of components in dilute solutions from specific conductivity measurements. The following ions are present in the reaction solution: Na^+, OH^- in CH_3COO^-, while ethyl acetate is a neutral molecule and does not contribute to conductivity. Therefore, conductivity can be expressed as:

$$\kappa = \lambda_{Na^+} c_{Na^+} + \lambda_{OH^-} c_{OH^-} + \lambda_{CH_3COO^-} c_{CH_3COO^-} \tag{3.1}$$

where: λ_{Na^+}, λ_{OH^-} and $\lambda_{CH_3COO^-}$ ionic conductivity of Na^+, OH^- and CH_3COO^- ions, c_{Na^+}, c_{OH^-} and $c_{CH_3COO^-}$ concentrations of Na^+, OH^- and CH_3COO^- ions.

Concentration of Na^+ ions does not change and is equal to the initial concentration of sodium hydroxide:

$$c_{Na^+} = c_{A0} \tag{3.2}$$

Concentration of CH_3COO^- ions is equal to the concentration of sodium acetate:

$$c_{CH_3COO^-} = c_C \tag{3.3}$$

Concentration of OH^- ions is initially equal to the concentration of Na^+ ions and decreases over time as the concentration of CH_3COO^- ions increases:

$$c_{OH^-} = c_{A0} - c_C \tag{3.4}$$

Taking into account all these terms for concentrations, equation (3.1) can be written:

$$\kappa = \lambda_{\mathrm{Na^+}} c_{\mathrm{A0}} + \lambda_{\mathrm{OH^-}} (c_{\mathrm{A0}} - c_{\mathrm{C}}) + \lambda_{\mathrm{CH_3COO^-}} c_{\mathrm{C}} \tag{3.5}$$

Rearranging this equation we can express it as the concentration of sodium acetate:

$$c_{\mathrm{C}} = \frac{c_{\mathrm{A0}} (\lambda_{\mathrm{Na^+}} + \lambda_{\mathrm{OH^-}}) - \kappa}{\lambda_{\mathrm{OH^-}} - \lambda_{\mathrm{CH_3COO^-}}} \tag{3.6}$$

The initial conductivity, κ_0, when we do not yet have sodium acetate in the reaction solution, is equal to:

$$\kappa_0 = c_{\mathrm{A0}} (\lambda_{\mathrm{Na^+}} + \lambda_{\mathrm{OH^-}}) \tag{3.7}$$

Therefore, we can write equation (3.6) in the form:

$$c_{\mathrm{C}} = \frac{\kappa_0 - \kappa}{\lambda_{\mathrm{OH^-}} - \lambda_{\mathrm{CH_3COO^-}}} \tag{3.8}$$

Difference of ionic conductivity of OH^- and CH_3COO^- ions is written by empirical expression taking into account the temperature correction factor:

$$c_{\mathrm{C}} = \frac{\kappa_0 - \kappa}{135 + 2{,}1\ (T - 18)} \tag{3.9}$$

where: T temperature in °C; (conductivity in $\mathrm{mS \cdot cm^{-1}}$).

When the reaction is completed, the concentration of sodium acetate is equal to the initial concentration of ethyl acetate:

$$c_{\mathrm{B0}} = \frac{\kappa_0 - \kappa_\infty}{135 + 2{,}1\ (T - 18)} \tag{3.10}$$

where: κ_∞ conductivity when the reaction is completed, and T temperature in °C; (conductivity in $\mathrm{mS \cdot cm^{-1}}$).

From equation (3.7) the initial concentration of sodium hydroxide can be expressed:

$$c_{\mathrm{A0}} = \frac{\kappa_0}{\lambda_{\mathrm{Na^+}} + \lambda_{\mathrm{OH^-}}} \tag{3.11}$$

The sum of ionic conductivities of Na^+ and OH^- ions is written by empirical expression taking into account the temperature correction factor:

$$c_{A0} = \frac{\kappa_0}{198 + 3,7\ (T - 18)} \tag{3.12}$$

where: T temperature in °C; (conductivity in $mS{\cdot}cm^{-1}$).

The equations for calculating the initial concentrations of sodium hydroxide and ethyl acetate and sodium acetate and sodium hydroxide in the steady state are:

$$c_{A0} = \frac{\kappa_0}{198 + 3,7\ (T - 18)} \tag{3.13}$$

$$c_{B0} = \frac{\kappa_0 - \kappa_\infty}{135 + 2,1\ (T - 18)} \tag{3.14}$$

$$c_C = \frac{\kappa_0 - \kappa}{135 + 2,1\ (T - 18)} \tag{3.15}$$

$$c_A = c_{A0} - c_C \tag{3.16}$$

where: κ_0 is the initial conductivity, κ conductivity, κ_∞ conductivity at the end of the reaction and T temperature; (conductivity in $mS{\cdot}cm^{-1}$).

The conversion of ethyl acetate is:

$$X_A = 1 - \frac{c_A}{c_{A0}} = \frac{c_C}{c_{A0}} \tag{3.17}$$

Theoretical value of concentration in plug flow reactor

The reaction rate equation of a second-order reaction is written as:

$$-r_A = -\frac{dc_A}{d\tau} = k\, c_A\, c_B \tag{3.18}$$

The concentrations of reactants are expressed:

$$c_A = c_{A0} - c_C \tag{3.19}$$

$$c_B = c_{B0} - c_C \tag{3.20}$$

If we integrate equation (3.6) and then rearrange it, we obtain an expression from which the concentration of sodium hydroxide in the steady state is calculated:

$$c_A = \frac{c_{A0}\,(c_{B0} - c_{A0})\,\mathrm{e}^{k\,(c_{A0} - c_{B0})\,\tau}}{c_{B0} - c_{A0}\,\mathrm{e}^{k\,(c_{A0} - c_{B0})\,\tau}} \tag{3.21}$$

The conversion of ethyl acetate is:

$$X_A = 1 - \frac{c_A}{c_{A0}} = \frac{c_C}{c_{A0}} \tag{3.22}$$

Theoretical value of concentration in continuous stirred tank reactor

The general reaction rate equation of a second-order reaction is written as:

$$-r_A = -\frac{\mathrm{d}c_A}{\mathrm{d}\tau} = k\,c_A\,c_B \tag{3.23}$$

From the mass balance for the continuous stirred tank reactor, we get:

$$(-r_A)\,V = F_{A0}\,X_A \tag{3.24}$$

where: F_{A0} is the molar flow.

Considering the equation (3.12) residence time can be expressed as:

$$\tau = \frac{V}{q_V} = \frac{V\,c_{A0}}{F_{A0}} = \frac{c_{A0}\,X_A}{-r_A} = \frac{c_{A0} - c_A}{-r_A} \tag{3.25}$$

Thus:

$$-r_A = \frac{c_{A0} - c_A}{\tau} \tag{3.26}$$

Considering equations (3.11) and (3.14) and the relationship:

$$c_B = c_{B0} - (c_{A0} - c_A) \tag{3.27}$$

we get the expression for the calculation of concentration of sodium hydroxide in steady state:

$$k\,\tau\,c_{\mathrm{A}}^{2} + c_{\mathrm{A}}\,(k\,\tau\,(c_{\mathrm{B0}} - c_{\mathrm{A0}}) + 1) - c_{\mathrm{A0}} = 0 \tag{3.28}$$

The conversion of ethyl acetate is:

$$X_{\mathrm{A}} = 1 - \frac{c_{\mathrm{A}}}{c_{\mathrm{A0}}} = \frac{c_{\mathrm{C}}}{c_{\mathrm{A0}}} \tag{3.29}$$

Theoretical value of concentration in cascade mixed flow reactor

To calculate the steady-state concentration of sodium hydroxide for an individual reactor in a cascade of continuous stirred tank reactors, we use equation (3.16), considering that the concentration at the outlet from the reactor is the same as the concentration at the inlet of the next reactor. First, calculate the concentration of sodium hydroxide at the outlet from the first reactor c_{A1} from equation (3.16), then use the following formula to calculate the concentration of ethyl acetate at the outlet from the first reactor c_{B1}:

$$c_{\mathrm{B1}} = c_{\mathrm{B0}} - (c_{\mathrm{A0}} - c_{\mathrm{A1}}) \tag{3.30}$$

These two concentrations (c_{A1} and c_{B1}) are the same as the concentrations at the inlet of the second reactor. Then, following the same procedure from equations (3.16) and (3.18), calculate the concentrations at the outlet from the second reactor (c_{A2} in c_{B2}), which are also the concentrations at the inlet to the third reactor. Then calculate all remaining concentrations for the entire cascade system.

The conversion of ethyl acetate is:

$$X_{\mathrm{A}} = 1 - \frac{c_{\mathrm{A}}}{c_{\mathrm{A0}}} = \frac{c_{\mathrm{C}}}{c_{\mathrm{A0}}} \tag{3.31}$$

Accessories and chemicals

- beakers,
- measuring cylinders,
- measuring flasks,
- EtAc,

- NaOH,
- thermometers,
- stirrer,
- conductivity meter,
- different continuous reactors.

Experimental procedure

Prepare 10 L of ethyl acetate solution with the concentration, $c = 0.06 \text{ mol}\cdot\text{L}^{-1}$ and 10 L of sodium hydroxide solution with the concentration, $c = 0.08 \text{ mol}\cdot\text{L}^{-1}$. Fill the containers with prepared solutions. Experiments will be conducted in plug flow, mixed flow and cascade mixed flow continuous reactors. The reactions will be conducted at constant flow $q_A = q_B = (5 - 8) \text{ L}\cdot\text{h}^{-1}$ and at room temperature. The reactors are filled with deionized water. Each reactor is equipped with a conductivity meter at the outlet of the reactor. Open the appropriate valves and set them to right position. At the same time start the measuring procedure in the program on a computer. Maintain a constant flow through the reactor to ensure a consistent residence time. Conductivity will be measured every 5 seconds. At the end of the experiment the values of the conductivity should be constant. Repeat the experimental procedure for all other continuous reactors.

Calculation and results

- calculate the initial concentrations of ethyl acetate and sodium hydroxide,
- plot κ regarding t for each reactor,
- create a table with the practical and theoretical values of conversions.

4. EXERCISE

Ethyl Acetate Saponification in Plug Flow Reactor

Purpose of the exercise

The purpose of the exercise is to perform the saponification of ethyl acetate with sodium hydroxide in plug flow reactor. The reaction can be written as:

$$\mathrm{CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH}$$

Theoretical background

The concentration of sodium hydroxide in the sample will be determined by re-titration and can be calculated using the following equation:

$$c_\mathrm{A} = \frac{c_\mathrm{NaOH}\,(V_\mathrm{HCl} - V_\mathrm{NaOH})}{V_\mathrm{HCl}} \tag{4.1}$$

where: c_NaOH is the concentration of sodium hydroxide used for titration V_NaOH volume of used sodium hydroxide, V_HCl volume of hydrochloric acid used to neutralize the sample.

The general equation for the reaction rate of a second-order reaction with respect to reactant A is written as:

$$-r_\mathrm{A} = -\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}\tau} = k\,c_\mathrm{A}^2 \tag{4.2}$$

where: c_A is the concentration of sodium hydroxide, τ residence time and k reaction rate constant. If equation (4.2) is integrated, we get an expression for calculating the reaction rate constant in a plug flow reactor:

$$k = \frac{1}{\tau\,c_\mathrm{A0}}\,\frac{(c_\mathrm{A0} - c_\mathrm{A})}{c_\mathrm{A}} \tag{4.3}$$

where: c_A0 is the initial concentration of sodium hydroxide.

The conversion of ethyl acetate is:

$$X_\mathrm{A} = 1 - \frac{c_\mathrm{A}}{c_\mathrm{A0}} \tag{4.4}$$

Activation energy

For the determination of the activation energy for selected reaction it is necessary that the reaction is carried out at least at three different temperatures. It is known that the temperature affects the reaction rate constant. Activation energy and pre-exponential factor are obtained from the Arrhenius equation:

$$k = k_0 \, \mathrm{e}^{-\frac{E_a}{R\,T}} \tag{4.5}$$

where: k_0 is the pre-exponential factor, R gas constant, T temperature and E_a activation energy.

Accessories and chemicals

- beakers,
- measuring cylinders,
- Erlenmeyer flasks,
- burette,
- EtAc,
- NaOH,
- HCl,
- stopwatch,
- plug flow reactor.

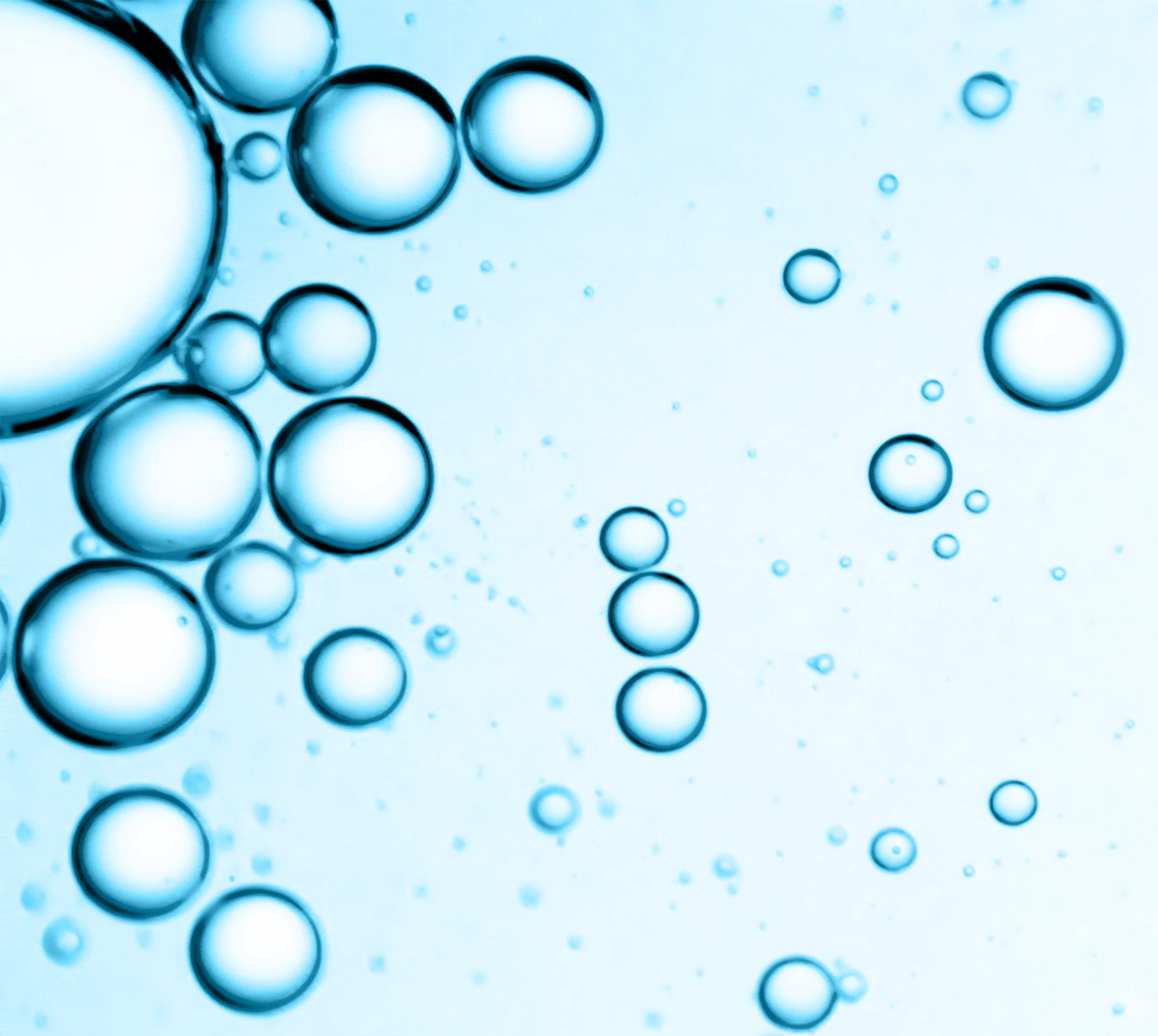
Experimental procedure

The experiments will be conducted in a continuous plug flow reactor with a volume of $V = 470$ mL. Prepare 10 L of sodium hydroxide solution with a concentration of $c_{A0} = 0.1$ mol·L^{-1} and 10 L of ethyl acetate solution with a concentration of $c_{B0} = 0.1$ mol·L^{-1}. Fill the tanks with the prepared solutions. In the meantime, prepare Erlenmeyer flasks for retitration. Put 10 mL of hydrochloric acid with a concentration of $c = 0.1$ mol·L^{-1} and 2-3 drops of the phenolphthalein indicator into each Erlenmeyer flasks. The burette should be filled with a sodium hydroxide solution with a concentration, $c = 0.1$ mol·L^{-1}.

We will perform the reactions at different flow rates, $q_A = q_B =$ (100, 60 and 20) mL·min^{-1} and at different temperatures, T = (25, 30 and 35) °C. Start the CET Tubular Reactor program and select Experiment with Heater, click Load. If the reactor system is properly connected to the PC then the Watchdog light will flash. By clicking on Setup, check whether the data capture is set to Automatic and the capture time to Continuous. Enter the concentrations of both reactants in the box. Before starting the reaction, the thermostatic liquid must be heated, thus set the desired temperature in the program on the computer by clicking on Control for automatic regulation (for example, Set Point = 25 °C). Click the Power On and then the Hot Water Circulator. Set the desired flow rates of both pumps. When the reactor is completely filled with the reaction medium, start data acquisition by clicking on the green Go button. If we want to monitor the data in tabular form, click on Table or in graphic form by clicking on Graph. Return to the view with the process diagram by clicking on the Diagram. When a steady state is established under certain experimental conditions and the conductivity no longer changes, 10 mL of the sample is pipetted into each of the prepared Erlenmeyer flasks. The unreacted sodium hydroxide in the sample will be neutralized by hydrochloric acid, which results in termination of the reaction. The excess hydrochloric acid is then titrated with sodium hydroxide. The procedure is repeated at all other flows and temperatures. Data capture is completed by clicking the red Stop button and the data is saved.

Calculation and results

- create a table with the concentrations of sodium hydroxide c_A, conversions X_A and reaction rate constants k at all experimental conditions,
- plot X_A regarding q,
- plot X_A regarding T,
- create a table with the reaction rate constants k, and their logarithm values $\ln k$, at each temperature T,
- plot Arrhenius plot,
- calculate pre-exponential factor, k_0 and activation energy, E_a.



5. EXERCISE

Ethyl Acetate Saponification in Batch and Continuous Stirred Tank Reactor

Purpose of the exercise

The purpose of the exercise is to perform the saponification of ethyl acetate with sodium hydroxide in batch and continuous mixed flow reactor. The reaction can be written as:

$$\mathrm{CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH}$$

Theoretical background

The concentration of sodium hydroxide in the sample will be determined by re-titration and can be calculated using the following equation:

$$c_\mathrm{A} = \frac{c_\mathrm{NaOH}\,(V_\mathrm{HCl} - V_\mathrm{NaOH})}{V_\mathrm{HCl}} \tag{5.1}$$

where: c_NaOH is the concentration of sodium hydroxide used for titration, V_NaOH volume of used sodium hydroxide, V_HCl volume of hydrochloric acid used to neutralize the sample.

The conversion of ethyl acetate is:

$$X_\mathrm{A} = 1 - \frac{c_\mathrm{A}}{c_\mathrm{A0}} \tag{5.2}$$

Batch reactor

Reaction order

The general equation for the reaction rate with respect to reactant A is written as:

$$-r_\mathrm{A} = -\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}\tau} = k\,c_\mathrm{A}^n \tag{5.3}$$

where: c_A is the concentration of sodium hydroxide, t time, k_t reaction rate constant and n reaction order. If we logarithm the equation 5.3 we get:

$$\ln\left(-\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}t}\right) = \ln k + n \ln c_\mathrm{A} \tag{5.4}$$

By plotting $\ln(-\mathrm{d}c_\mathrm{A}/\mathrm{d}t)$ as a function of $\ln c_\mathrm{A}$ we can determine $\log k$ from the intercept of the line and n from the slope of the line.

Reaction order can be determined from the experimental data by checking the linearity of the dependence of various concentration terms as a function of time. Table 5.1 contains the expressions for calculating the reaction rate, its integrated form and the dependence of the concentration terms for different reaction order.

Table 5.1: Reaction order and reaction rate equations.

Reaction order	Rate equation	Integrated from	Linear dependance	Slope	Unit of reaction rate constant
0.	$-r_A = k$	$c_{A0} - c_A = k\,t$	$c_A = f(t)$	$-k$	mol·L⁻¹·min⁻¹
1.	$-r_A = k\,c_A$	$\ln\frac{c_{A0}}{c_A} = k\,t$	$\ln c_A = f(t)$	$-k$	min⁻¹
2.	$-r_A = k\,c_A^2$	$\frac{1}{c_A} - \frac{1}{c_{A0}} = k\,t$	$\frac{1}{c_A} = f(t)$	k	L·mol⁻¹·min⁻¹

Continuous stirred tank reactor

The general equation for the reaction rate of a second-order reaction with respect to reactant A is written as:

$$-r_A = -\frac{dc_A}{d\tau} = k\,c_A^2 \tag{5.5}$$

where: c_A is the concentration of sodium hydroxide, τ residence time and k reaction rate constant. From the mass balance for continuous stirred tank reactor, we get:

$$(-r_A)\,V = F_{A0}\,X_A \tag{5.6}$$

where: F_{A0} is the molar flow. Taking into account equation (5.6), the residence time is expressed as:

$$\tau = \frac{V}{q} = \frac{V\,c_{A0}}{F_{A0}} = \frac{c_{A0}\,X_A}{-r_A} = \frac{c_{A0} - c_A}{-r_A} \tag{5.7}$$

where: c_A is the concentration of sodium hydroxide.

Thus:

$$-r_A = \frac{c_{A0} - c_A}{\tau} \tag{5.8}$$

Taking into account equations (5.5) and (5.8), we can determine the reaction rate constant in a continuous stirred tank reactor in a steady state:

$$k = \frac{1}{\tau} \frac{(c_{A0} - c_A)}{c_A^2} \tag{5.9}$$

Activation energy

For the determination of the activation energy for selected reaction it is necessary that the reaction is carried out at least at three different temperatures. It is known that the temperature affects the reaction rate constant. Activation energy and pre-exponential factor are obtained from the Arrhenius equation:

$$k = k_0 \, e^{-\frac{E_a}{R\,T}} \tag{5.10}$$

where: k_0 is the pre-exponential factor, R gas constant, T temperature and E_a activation energy.

Accessories and chemicals

- beakers,
- measuring cylinders,
- measuring flasks,
- Erlenmeyer flasks,
- containers,
- burette,
- EtAc,
- NaOH,
- HCl,
- stopwatch,
- batch and continuous stirred tank reactor.

Experimental procedure

Batch reactor

Experiments will be conducted in a batch reactor. Prepare 1 L of sodium hydroxide solution with a concentration of c_{A0} = 0.1 mol·L^{-1} and 1 L of ethyl acetate solution with a concentration of c_{B0} = 0.1 mol·L^{-1}. Prepare Erlenmeyer flasks for retitration. Put 10 mL of hydrochloric acid with a concentration of c = 0.1 mol·L^{-1} and 2-3 drops of the phenolphthalein indicator into each Erlenmeyer flask. Fill the burette with a sodium hydroxide solution with a concentration of c = 0.1 mol·L^{-1}.

The reaction will be conducted at a constant temperature between T = (25 – 35) °C. Fill the batch reactor with 600 ml of ethyl acetate solution. Start the CEM Continuous Stirred Tank Reactor program and select Experiment with Heater, click Load. If the reactor system is properly connected to the PC then the Watchdog light will flash. By clicking on Setup, check whether the data capture is set to Automatic and the capture time to Continuous. Enter the concentrations of both reactants in the box. Before starting the reaction, the thermostatic liquid must be heated, thus set the desired temperature in the program on the computer by clicking on Control for automatic regulation (for example, Set Point = 25 °C). Click the Power On and then the Hot Water Circulator. When the temperature is reached, start capturing data by clicking on the green Go button. Start the reaction by pouring 600 mL of the sodium hydroxide solution as quickly as possible into the batch reactor to the ethyl acetate solution and start to measure the time. Set the desired stirring speed (Stirrer Control). At the same time, take the first sample (10 mL) and put it in the prepared Erlenmeyer flask. Record the time when the last drop of the sample falls into the Erlenmeyer flask. Then take samples at various time intervals, initially more often, the first five samples consecutively, then every 2 minutes. The unreacted sodium hydroxide in the sample will be neutralized by the hydrochloric acid, which results in termination of the reaction. The excess hydrochloric acid is then titrated with sodium hydroxide. Record time and consumption - volume during titration. The experiment is carried out for 20 minutes. If we want to monitor the data in tabular form click on Table or in graphic form by clicking on Graph. Return to the view with the process diagram by clicking on the Diagram. Data capture is completed by clicking the red Stop button and the data is saved.

Continuous stirred tank reactor

Experiments will be conducted in a continuous stirred tank reactor with volume, $V = 1500$ mL. Prepare 10 L of sodium hydroxide solution with a concentration of $c_{A0} = 0.1$ mol·L^{-1} and 1 L0 of ethyl acetate solution with a concentration of $c_{B0} = 0.1$ mol·L^{-1}. Prepare Erlenmeyer flasks for retitration. Put 10 mL of hydrochloric acid with a concentration of $c = 0.1$ mol·L^{-1} and 2-3 drops of the phenolphthalein indicator into each Erlenmeyer flask. Fill the burette with a sodium hydroxide solution with a concentration of $c = 0.1$ mol·L^{-1}.

The reactions will be conducted at different temperatures, $T = (25, 30$ and $35)$ °C and constant flow rate, $q_A = q_B = 100$ mL·min^{-1}. Start the CEM Continuous Stirred Tank Reactor program and select Experiment with Heater, click Load. If the reactor system is properly connected to the PC then the Watchdog light will flash. By clicking on Setup, check whether the data capture is set to Automatic and the capture time to Continuous. Enter the concentrations of both reactants in the box. Before starting the reaction, the thermostatic liquid must be heated, thus set the desired temperature in the program on the computer by clicking on Control for automatic regulation (for example, Set Point = 25 °C). Click the Power On and then the Hot Water Circulator. Set the desired stirrer speed (Stirrer Control). When the temperature is reached, start capturing data by clicking the green Go button. Set the desired flow rates of both pumps. At the same time, take the first sample (10 mL) and put it in the prepared Erlenmeyer flask. Record the time when the last drop of the sample falls into the Erlenmeyer flask. Then take samples at various time intervals, initially more often, the first five samples consecutively, then every 2 minutes. Samples are taken until a steady state is reached and the conductivity no longer changes. When the steady state is reached, take 3 more samples in a row. The unreacted sodium hydroxide in the sample will be neutralized by the hydrochloric acid and consequently the reaction will stop. The excess hydrochloric acid is then titrated with sodium hydroxide. Record the time and consumption - volume during titration. If we want to monitor the data in tabular form click on Table or in graphic form by clicking on Graph. Return to the view with the process diagram by clicking on the Diagram. Increase the temperature and wait until the steady state is restored. Take 3 samples in a row. Increase the temperature again and wait until a steady state is established. Take 3 more samples in a row. Data capture is completed by clicking the red Stop button and the data is saved.

Calculation and results

- create a table with the t and c_A,
- create a table with the c_A, $\ln c_A$ and $1/c_A$, regarding t,
- plot c_A regarding t,
- plot $\ln c_A$ regarding t,
- plot $1/c_A$ regarding t,
- write down reaction order, n, and reaction rate constant, k,
- create a table with the reaction rate constants, k, and their logarithm values, $\ln k$, at each temperature, T,
- plot Arrhenius plot,
- calculate pre-exponential factor, k_0 and activation energy, E_a.

Suggested Additional Study Literature

1. Levenspiel Octave, Chemical Reaction Engineering, Third Edition, Wiley, 1998.
2. Instruction manual for CEB-MKIII Transparent batch reactor, Armfield.
3. Instruction manual for CET-MKII Tubular reactor, Armfield.
4. Instruction manual for CEM-MKII Continuous stirred tank reactor, Armfield.

CHEMICAL REACTION ENGINEERING I: MANUAL FOR PERFORMING LABORATORY EXERCISES

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