INTERCOMPANY MEMORANDUM

CAL CHEM CORPORATION

To: CHE Seniors                                  Date: Fall Quarter
From: CHE faculty                              File: CHE 435
      Laboratory Managers

Subject: Batch Reactor Kinetic Analysis

Our process engineers are currently working on developing a process that has an undesirable side reaction, the saponification of ethyl acetate. They would like to know the kinetics of the reaction since this reaction is of considerable importance in their process. We want your group to find out as much as possible in the allotted time. If possible find the overall reaction order, the reaction order with respect to each of the reacting species, the reaction rate constant, and the temperature dependency of this rate constant. In your report please verify your conclusions with information available in the literature.

Our technician has suggested the following procedure:

Prepare a 0.01N solution of NaOH and ethyl acetate. Place about 500 ml of NaOH and 500 ml of ethyl acetate into a water bath maintained at a constant temperature. Do not combine the reactants at this time. This step is only to insure that when the reactants are combined at a later time, the system will be at a constant uniform temperature.

Conductivity measurements may be used to follow the progress of the reaction. One may show that the ratio of the difference of conductivity at time zero and at time t to the difference of conductivity at time zero and at reaction completion is directly proportional to the extent of reaction because the conductivities of ethyl acetate and ethyl alcohol may be ignored. Starting and final conductivities are best found by extrapolation.

Make sure you properly calibrate the probe, handle the probe with care, and properly clean the probe at the end of the experiment.
Batch Reactor Kinetic Analysis

The saponification of ethyl acetate (CH$_3$CO$_2$C$_2$H$_5$) with dilute sodium hydroxide (NaOH) is a second-order, irreversible reaction which can be represented by the following equation:

$$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{NaOH} \rightarrow \text{C}_2\text{H}_5\text{CO}_2\text{Na} + \text{CH}_3\text{OH}$$  \hspace{1cm} (1)

In this reaction, the OH$^-$ ion is the most highly conductive species therefore the conductivities of ethyl acetate, C$_2$H$_5$CO$_2$Na, and ethyl alcohol may be ignored. The conductivity meter used in our lab (Cole-Palmer Model 19100-00) is designed to display the conductivity of the solution in terms of the specific conductivity, $C$, which is related to the NaOH concentration by the following equation:

$$\frac{C - C_\infty}{C_0 - C_\infty} = \frac{C_A - C_{A\infty}}{C_{A0} - C_{A\infty}}$$  \hspace{1cm} (2)

where

- $C$ = specific conductivity at time $t$
- $C_0$ = specific conductivity at time $t = 0$
- $C_\infty$ = specific conductivity at time $t = \infty$
- $C_A$ = NaOH concentration at time $t$
- $C_{A0}$ = NaOH concentration at time $t$
- $C_{A\infty}$ = NaOH concentration at time $t = \infty$

For the saponification reaction (1), $C_{A\infty} \rightarrow 0$ as $t \rightarrow \infty$, if the reaction is carried out in a constant volume batch reactor

$$\frac{C_A}{C_{A0}} = \frac{N_A}{N_{A0}} = \frac{C - C_\infty}{C_0 - C_\infty} = 1 - X$$  \hspace{1cm} (3)

where $X$ is the fractional conversion of sodium hydroxide. Eq. (3) can also be arranged to

$$X = \frac{C_0 - C}{C_0 - C_\infty}$$

For a second order reaction rate with equimolar concentration, the fractional conversion is related to the reaction rate constant $k$ by

$$\frac{X}{1 - X} = C_{A0}kt$$  \hspace{1cm} (4)

The temperature dependence of the reaction rate constant could be correlated by the Arrhenius equation

$$k = Ae^{-E/RT}$$  \hspace{1cm} (5)

where $A$ = preexponential factor or frequency factor
E = activation energy, J/mol or cal/mol
R = gas constant = 8.314 J/mol*K = 1.987 cal/mol*K
T = absolute temperature, K

Recommended Procedure

**Batch reactor**

The apparatus in our lab can be run as a batch or a continuous stirred tank reactor. For the batch mode, pour about 500 ml each of 0.01N NaOH solution and 0.01N ethyl acetate solution into the vessel using a funnel. The vessel comprises of a glass cylinder with a steel base and a removable PVC top cover for access and cleaning purposes. Liquids with the reactor are mixed by means of a motor driven stirrer and a removable baffle assembly.

Temperature of the liquid in the reactor is controlled by hot water circulating through a coil immersed in the reactor. Initially cold water is admitted into the heater tank through the solenoid valve that closes automatically when the operating level is reached. The water is then heated by a heating element in the tank and circulated to the reactor vessel by the pump, and back to the tank by the return pipe.

When the controller is set in the cooling mode, the solenoid valve opens and cold water is pumped directly to the reactor vessel and hot water is discharged through the overflow pipe to drain. Thus, the overflow pipe only operates when the reactor is in the cooling mode. On the controller an integral meter indicates the deviation from the set temperature. The top red light indicates that the controller is connected to the mains supply. The bottom red light indicates that power is being supplied to the heater. The control panel carries a main switch along with stirrer buttons for each of the feed pumps and the stirrer motor. Stirrer speed is controlled by a variable transformer. An indicator lamp on the control panel gives visual warning of inadequate water supply to the heating and cooling unit.

**Conductivity Meter**

![Figure 1. Schematic of Cole-Palmer Dual Scale Analog Conductivity Meter](image)
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A. Analog Display: From 0 to 1.1 Conductance, and from $\infty$ to .0 Resistance.
B. Mechanical Zero for analog display
C. Standardize Control: master calibration control
D. Cell Connector
E. Range switch: allows operator to select any one of six ranges.
F. Power switch and Battery Check
H. Recorder output: on model 19100-20 only.

Figure 1 shows the Cole-Palmer Dual Scale Analog Conductivity Meter Model 19100-00 used in our lab. The suggestions to carry out this experiment are reproduced from the Conductivity Meter manual.

Set-Up Procedure

The first step in using the conductivity meter, before the power is switched on, is to adjust the mechanical (B) by setting the needle to the “0” on the conductance scale. The clean and dry conductivity cell is then connected to the conductivity meter and power (F) and ATC (G) switch turned to ON position. The power switch is turned in BATT CK position to check the condition of the battery in the conductivity meter. The reading on the conductivity scale will give the reading above 7 to indicate good battery. If the reading is below 7, the battery needs to be replaced.

Calibration

The conductivity cell must be calibrated before use to obtain good and reproducible data with the conductivity meter. The calibration is done with 0.005M KCl standard solution with known conductivity of 0.718 mS/cm. To minimize the error, it is best to calibrate the cell using a standard solution with a conductivity within the range for which the cell is to be used.

The cell is immersed in the sample solution and with the conductivity scale set to the 1 mS range, the conductivity is adjusted to 0.718 by the standardize control knob (C).

The cell constant is determined by turning the ATC switch to the STANDARDIZE position. The value of the cell constant is displayed on the conductivity scale. The conductivity meter used in this project has the cell constants of approximately 10 cm$^{-1}$.

The conductivity meter is designed to display the conductivity of the solution in terms of the specific conductivity, C, product of the conductivity and the cell constant.

Conductivity Measurements

The conductivity meter is ready for measurements only after the zero has been adjusted and the conductivity cell calibrated. The 500 ml of 0.01 M solution of NaOH and ethyl acetate are prepared and mixed together in a batch reactor at a constant temperature (Note: you need to determine the appropriate total liquid volume required for the experiment). The conductivity cell is then placed into the reaction mixture that is constantly stirred within the reactor. Appropriate mixing is essential for the success of the measurements. In a few seconds, the cell temperature equals the mixture temperature, and the conductivity can be read from the display once the needle stabilizes. One must avoid contact between the stirrer and the cell to prevent possible damage of the cell.
Once the conductivity cell is immersed into the solution, the appropriate conductivity range is selected (E). The initial conductivity range selected in this case is 10 mS, measuring from 0 to 11 mS. As the measured conductivities decrease to 1 mS, the next conductivity range of 1 mS is selected. Conductivity measurements are to be taken at 1, 2, 3, 4, 5, 10, 20, 25, … minutes. After the measurement is taken, the cell is to be removed from the solution, and the excess solution should be shaken off. The cell is to be cleansed with a mild liquid detergent and rinsed with distilled water. The cell must not be touched or wiped off.

**Minimum Data Analysis**

1. Carry out the reaction (1) at a minimum of three temperatures.

2. Extrapolate or curve fit the data to obtain \( C_0 \) and \( C_\infty \).

3. Derive\(^{[2]}\) Eq. (4) and a similar equation for the case when the concentrations of the two reactants are not equal.

4. Plot Eq. (4) or a similar expression to obtain the reaction rate constant.

5. Determine the values of A and E in Eq. (5).

**References**