KINETICS OF HYDROLYSIS OF ACETIC ANHYDRIDE BY IN-SITU FTIR SPECTROSCOPY

An Experiment for the Undergraduate Laboratory

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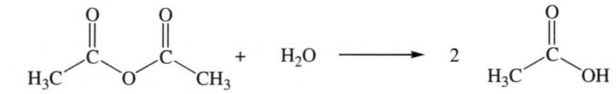
The senior-level chemical engineering undergraduate laboratory course at the University of Connecticut consists of two four-hour labs per week, during which groups of three to four students typically perform five experiments during the course of the semester. Each experiment is studied for either one or two weeks, depending on its complexity and the scale of the equipment. The students are given only the general goals for each experiment and are required to define their own objectives, to develop an experimental plan, to prepare a pre-lab report (including a discussion of safety measures), to perform the experiments and analyze the data, and to prepare group or individual written and/or oral reports.

One or two of the experiments in this course involve reaction kinetics. Over the years, we have encountered some challenges with reaction kinetics experiments, including inaccurate, tedious, and/or outdated methods for measuring concentrations of reactants or products, and very long or very short reaction times that make it difficult to monitor concentrations with current conventional methods.

We developed a reaction engineering experiment that employs *in-situ* Fourier Transfer Infrared (FTIR) spectroscopy for monitoring concentrations. The FTIR is a nondestructive technique that is increasingly employed by chemists and chemical engineers to obtain real-time data by *in-situ* monitoring. Since no sampling is required, this analytical technique allows the reaction kinetics to be observed under experimental conditions without disturbing the reaction mixture. The FTIR provides an effective but expensive analytical capability.

The hydrolysis of acetic anhydride (Ac_2O) to acetic acid (AcOH) was selected as the model reaction.



Quite a few studies have been reported in the literature on the kinetics of hydrolysis of acetic anhydride.[1,2,4,5] Eldridge and Piret[4] obtained the pseudo-first-order reaction rate constant using a batch reactor. To determine the acetic anhydride concentration, samples from the reactor were withdrawn into tared flasks containing 15-20 times the quantity of saturated aniline-water required to react with the sample. Since the anhydride rapidly acetylates the aniline, producing acetanilide and acetic acid, the samples were then titrated to determine the concentration of acetic acid. In another study, Shatyski and Hanesian[5] determined the kinetics of the above reaction by using temperature-vs-time data obtained under adiabatic conditions in a batch reactor.

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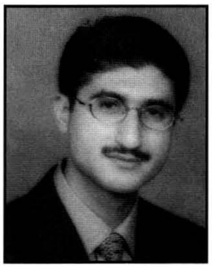

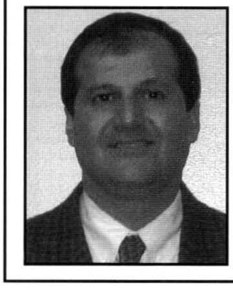

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For this laboratory, the reaction is carried out in a batch reactor at a minimum of three different temperatures. The concentration of acetic anhydride is measured as a function of time using *in-situ* FTIR spectroscopy. The data are then analyzed to determine the reaction order and the rate constant for this reaction. The resulting rate equation is used to predict the performance of a semibatch reactor, which is then compared to experimental data. This experiment requires three laboratory periods if the students construct the calibration curve themselves—otherwise, the teaching assistant can do the calibrations and it requires only two laboratory periods.

The hydrolysis of acetic anhydride reaction is a suitable reaction for many reasons. The final reaction product is a harmless acetic acid solution with concentrations in water ranging from 8 to 20 vol %. As with most chemicals, however, acetic anhydride and acetic acid should be handled in the hood. Safety glasses are needed when handling concentrated or moderately concentrated acid solutions. Butyl rubber or neoprene gloves should be used when handling concentrated solutions of acetic acid. Contact with eyes or skin should be avoided. Furthermore, both the reactant (acetic anhydride) and the product (acetic acid) can be monitored. The IR spectra of the reactants and the product (see Figure 1) indicate that each species has its own distinctive absorption peaks that are not obscured by those of the other two species. In addition, the rate of the reaction is such that a few experiments can be carried out in a four-hour laboratory period.

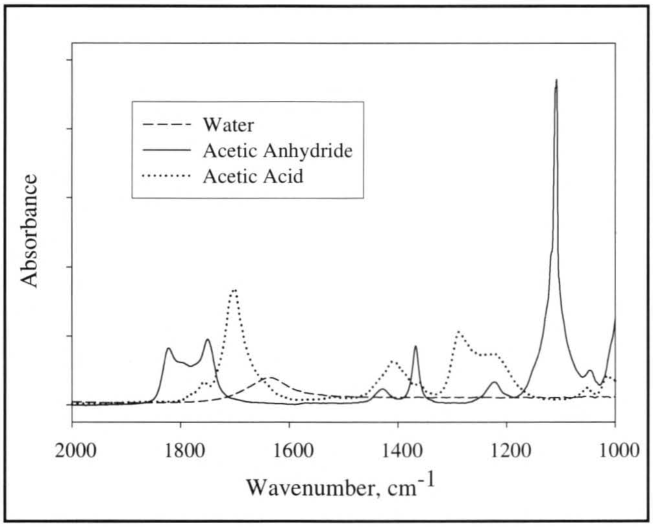

Figure 1. *IR spectra of pure water, acetic anhydride, and acetic acid.*

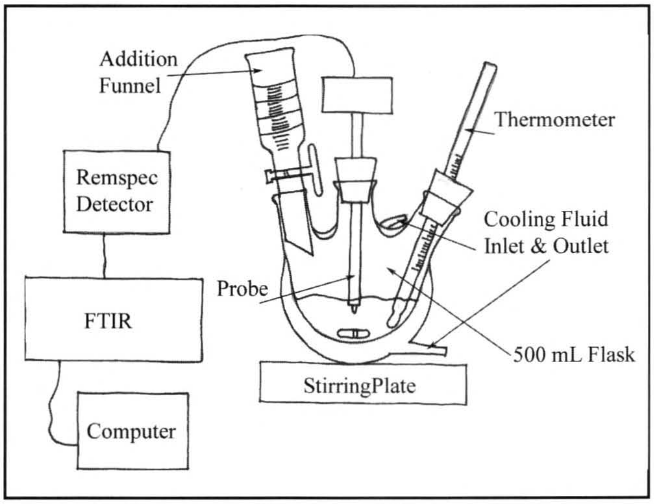

Figure 2. *Schematic diagram of the experiment setup.*

THE EXPERIMENT SETUP

A schematic diagram of the laboratory apparatus is shown in Figure 2. The reactor used in the experiment is a three-necked, 500-mL jacketed flask equipped with a magnetic stirrer. Water is circulated through the jacket to keep the reaction mixture at a constant temperature. A thermometer is fitted into one of the side necks of the flask and immersed in the reaction mixture. A mid-IR probe consisting of a zinc selenide ATR (attenuated total reflectance) crystal is fitted into the middle neck of the flask and submerged into the reaction mixture. The probe is connected to a Remspec mid-IR fiber-optic system comprising a bundle of 19 optical fibers, which transmits in the mid-IR range, 5000-900 cm^{-1}. Seven of these fibers are attached to a signal-launch module attached to the collimated external beam port of a Bruker Vector 22 FTIR spectrometer; twelve fibers are attached to an external liquid-nitrogen-cooled MCT detector fitted with specialized optics to optimize capture of the mid-IR signal from the end of the fiber bundle. The data are processed using computer software to obtain the IR absorption spectra.

For batch operation, the reactant (acetic anhydride) is introduced at initial time through a glass stopper that is fitted into the open neck of the reaction flask. For semibatch operation, a graduated addition funnel is fitted to the neck that can be calibrated to add acetic anhydride to the flask at a desired rate. The reactor is initially filled with a known quantity of water at the beginning of each experiment.

PROCEDURE

Before acquiring IR spectra during the reaction, a background spectrum of the empty reactor with optical fibers attached is acquired. For each experiment, 150 ml of distilled water is placed in the reactor. After heating or cooling the reactor to the desired temperature, a background spectrum is acquired again with the probe immersed in water.

For the batch mode, 10 ml of acetic anhydride is added to the stirred reactor, and the reactor is sealed with a glass stopper. The spectra are acquired using the repeated measurements option enabled by the software controlling the FTIR. The settings are adjusted for the acquisition of a spectrum every 50 seconds for 35 minutes. Spectral scans are taken at 4 cm^{-1} resolution and signal averaged over 32 scans. The absorbances of the selected peaks are measured from the individual spectra. It takes around 30 seconds for the 32 scans to be acquired.

Care should be exercised in selecting the operating conditions or the scan number to make sure that the concentration does not change significantly during the acquisition of each spectrum. For example, at the beginning of the reaction at 35°C, the concentration of acetic anhydride changes by 11% during the acquisition of the second spectrum (50-80 s).

For the semibatch reactor operation, an addition funnel is placed in the unoccupied neck. The acetic anhydride addition rate can be set between 2 to 5 ml/min. Once the first drop hits the water, the repeated measurements function is activated so that a spectrum is acquired every 50 seconds for one hour. The level in the addition flask is read at various times to determine the rate of addition as a function of time. The reaction mixture's temperature is recorded manually with each IR spectra acquired or as needed.

THEORY

For a constant-volume batch reactor, the rate of appearance of reactant A (acetic anhydride), r_A, is given by

$$r_A = \frac{dC_A}{dt} \tag{1}$$

where r_A can be expressed as

$$-r_A = kC_A^n C_B^m \tag{2}$$

where k is the reaction rate constant, n and m are the reaction orders with respect to species A (acetic anhydride) and B (water), respectively. Since water is in excess, C_B remains essentially unchanged during the course of the reaction, and

$$-r_A = k'C_A^n \tag{3}$$

where k' is a pseudo rate constant

$$k' = kC_B^m \approx kC_{B0}^m \tag{4}$$

The specific reaction rate, k, is a function of reaction temperature and is given by the Arrhenius equation

$$k = Ae^{-E/RT} \tag{5}$$

where A is a pre-exponential factor, E is the activation energy for the reaction, and T is the absolute temperature.

The reaction order and rate constant can be determined by the integral method of analysis.[3] In this method, the rate expression is guessed and the differential equation used to model the batch system is integrated. If the assumed order is correct, the appropriate plot (determined from the integration) of concentration-time data should be linear. For a zero order reaction with $-r_A = k$, integration of Eq. (1) yields

$$C_A = C_{A0} - kt \tag{6}$$

For the first-order case where $-r_A = kC_A$, integration of Eq. (1) yields

$$\ell n \frac{C_{A0}}{C_A} = kt \tag{7}$$

For the case where $-r_A = kC_A^2$, integration of Eq. (1) yields

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt \tag{8}$$

The differential method can also be used to analyze the rate data.[3] In this method, the reaction rate at each concentration is determined by differentiating concentration-versus-time data. By combining the mole balance (Eq. 1) with the rate law (Eq. 3), we obtain

$$-\frac{dC_A}{dt} = kC_A^n \tag{9}$$

Taking the natural logarithm of both sides of Eq. (9) gives

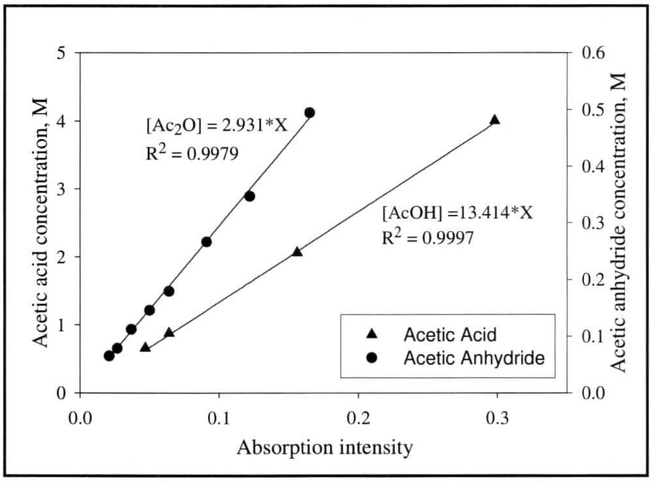

Figure 3. *Calibration curves of acetic anhydride and acetic acid.*

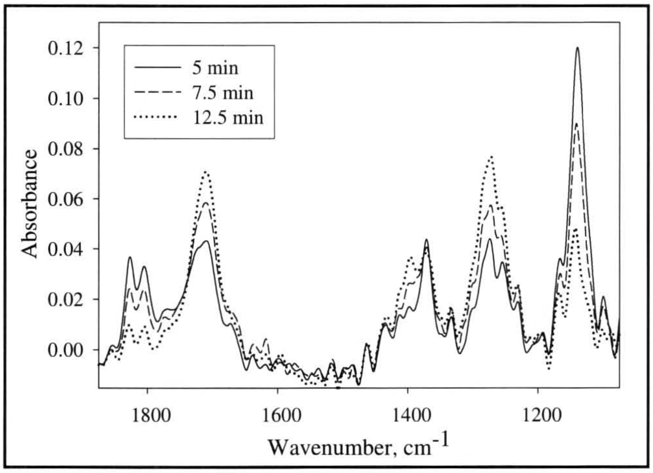

Figure 4. *The hydrolysis of acetic anhydride at different times [the acetic anhydride concentration is decreasing (1107 cm^{-1}) and that of acetic acid is increasing (1287 cm^{-1})].*

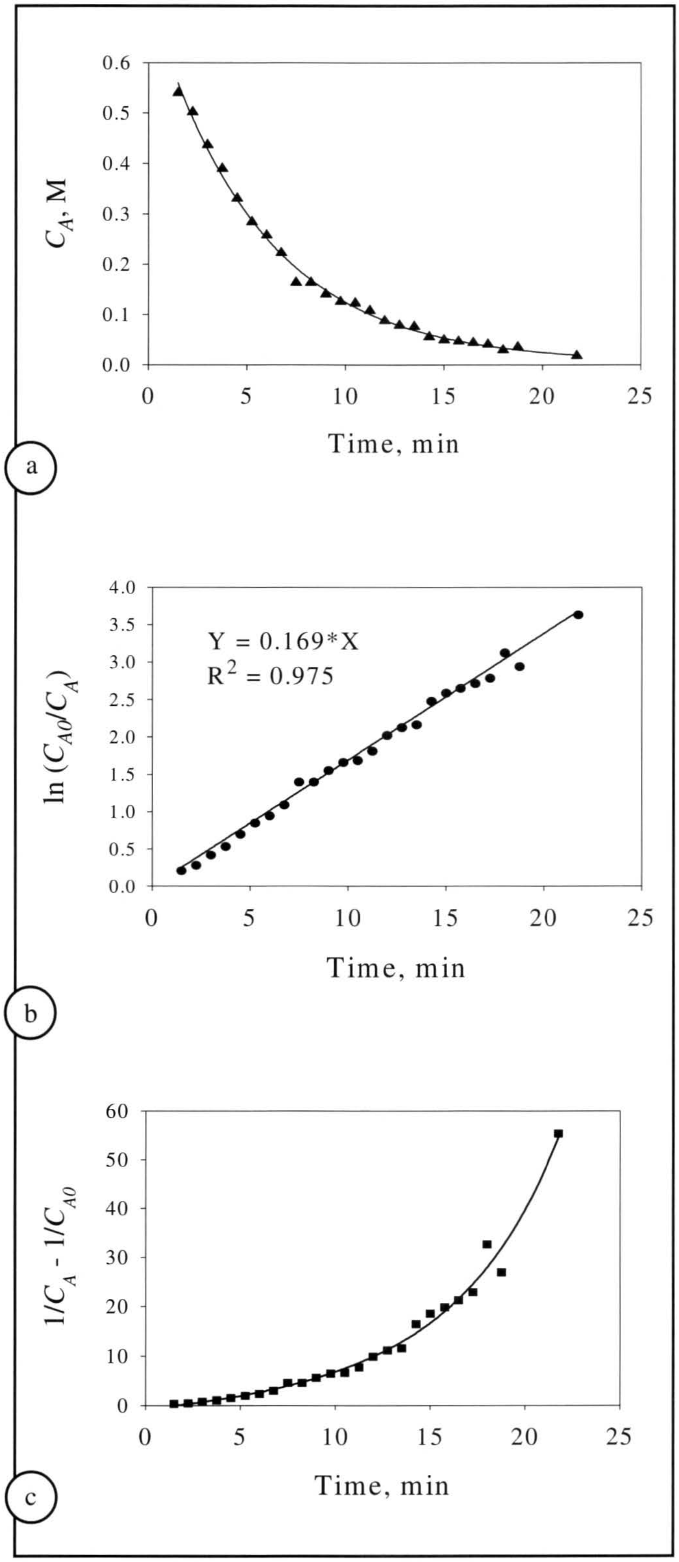

Figure 5. *Plots of the appropriate concentration function vs. time (a) zero order, (b) first order, and (c) second order reaction with respect to acetic anhydride (integral method). Data acquired at 25°C.*

$$\ell n\left(-\frac{dC_A}{dt}\right) = \ell n(k) + n\,\ell n\,C_A \qquad (10)$$

The slope of a plot of $\ell n(-dC_A/dt)$ vs. $(\ell n\,C_A)$ is the reaction order.

For the semibatch reactor where species A is being added to the system with a concentration of C_{A0}, the following relation can be derived from the mole balance relationship:

$$V\frac{dC_A}{dt} + C_A\frac{dV}{dt} = r_A V + v_0 C_{A0} \qquad (11)$$

where ν_0 is the volumetric flow rate into the system and V is the volume of the reacting mixture and is a function of time.

LAB SESSIONS AND RESULTS

Laboratory Period 1: Calibration Curve

In this session, the students learn how to operate the FTIR spectrometer and acquire data. Before they construct a calibration curve, IR spectra of the pure reactants (water and acetic anhydride) and the product (acetic acid) are acquired. The three spectra are compared, and the compounds that would be monitored along with their distinctive bands are selected (see Figure 1). Since water is present in excess, its concentration is not monitored. The concentration of acetic anhydride is monitored via the band at 1107 cm^{-1} associated with the stretching of C-O-C bond because it's the strongest peak and also does not overlap with the other peaks. The peaks due to carbonyl could also be monitored (1821 or 1750 cm^{-1}). The concentration of acetic acid is monitored via its C-OH absorption peak at 1287 cm^{-1} even though other peaks can also be used, *e.g.*, the carbonyl peak at 1703 cm^{-1}, which is the strongest peak in the acetic acid spectrum, or the peak at 1407 cm^{-1}. The peak at 1287 cm^{-1} does not overlap with the other peaks, however.

The calibration curve for the concentration of acetic acid solution in water vs. its absorption intensity is obtained by acquiring the spectra of solutions with known concentrations (*e.g.*, 0.6 M, 1.0 M, 2.0 M, and 4.0 M), as shown in Figure 3. It is not trivial to obtain a similar calibration curve for acetic anhydride, for it readily reacts with water. It is possible, however, to obtain a calibration curve for acetic anhydride using the calibration curve for acetic acid. At room temperature, 12 ml of acetic anhydride is added to 150 ml of water. The spectra are acquired every 2.5 minutes (see Figure 4). In each spectrum, the concentration of acetic acid is determined by measuring the absorbance of the designated peak and using the calibration curve. Given the reaction stoichiometry and the initial concentration, the acetic anhydride concentration can be calculated. Accordingly, a calibration curve for concentration of acetic anhydride vs. absorption intensity of the assigned band is constructed, as shown in Figure 3. Students are expected to determine the ranges in which the calibration curves for both acetic anhydride and acetic acid should be obtained.

The calibration curves are obtained at room temperature and are assumed to be valid over the range of temperatures at which the experiments were carried out. It is also assumed that the calibration of acetic acid in water solution is not affected by the presence of a third species (acetic anhydride) in the solution. Furthermore, it is possible to base the calculations only on measurements of the AcOH concentration and then back calculating the Ac_2O concentration without the need to obtain a calibration curve for the latter.

Laboratory Period 2: Isothermal Batch Reactor

Once the calibration curves are obtained, experiments are carried out in a batch reactor to determine the rate expression. Specifically, the hydrolysis of acetic anhydride in the presence of excess water (78.3:1 H_2O/Ac_2O) mol ratio, or 15:1 vol ratio) is carried out isothermally at room temperature (25°C). The concentrations of acetic anhydride and acetic acid are measured as a function of time. The concentration of acetic anhydride through the course of the reaction is shown in Figure 5(a). The data collected are analyzed using the integral method. The plot of C_A vs. time, as shown in Figure 5(a), and that of $(1/C_A - 1/C_{A0})$ vs. time, as shown in Figure 5(c), are not linear, indicating that the reaction is neither zero nor second order with respect to acetic anhydride. As Figure 5(b) illustrates, the plot of $\ell n(C_{A0}/C_A)$ as a function of time is linear, which suggests that the rate law is first order with respect to acetic anhydride concentration under given reaction conditions of excess water. The slope represents the rate constant, k. The rate constant is found to be 0.169 ± 0.0047 min^{-1} at 25°C, which is 7% higher compared to that reported in the literature,[4] which is 0.158 min^{-1} at the same temperature. The same reaction is repeated at temperatures of 15, 20, and 35°C. The data show the reaction is first order at all temperatures studied and the rate constants are found to be 0.0631, 0.0924, 0.2752 min^{-1} at 15, 20, and 35°C, respectively.

According to the Arrhenius equation (Eq. 5), a plot of $\ell n(k)$ vs. $1/T$ should be a straight line and the slope is proportional to the activation energy. Thus, knowing the reaction rate constant at four different temperatures, the students determine the activation energy and the pre-exponential factor. Once these values are known, k at any temperature could be determined using the Arrhenius equation. The pre-exponential factor is found to be $3.19*10^8$ min^{-1} and the activation energy to be 53,408.3 J/mol (see Figure 6). The average activation energy reported in the literature[5] is 50,241.6 J/mol, which differs by -5.9% from the value reported by the students.

The differential method can also be used to analyze the data collected. For instance, the data collected for the reaction at 15°C are analyzed to obtain the reaction order and the reaction rate constant. Only the data for conversion between 15% and 85% are used to increase the accuracy of the analy-

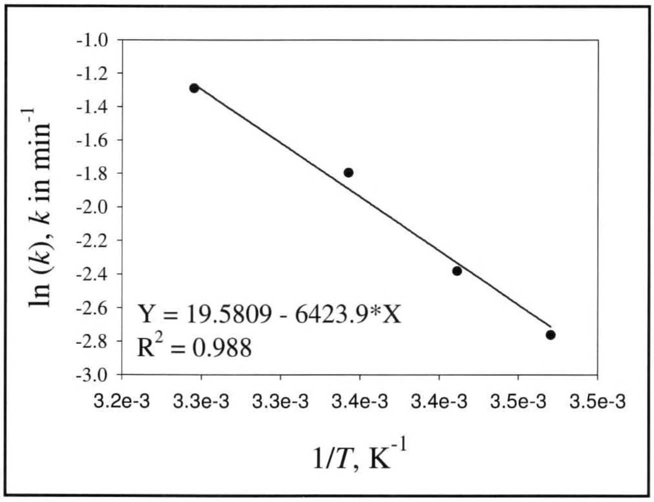

Figure 6. *Determination of the activation energy and the pre-exponential factor using the Arrhenius equation.*

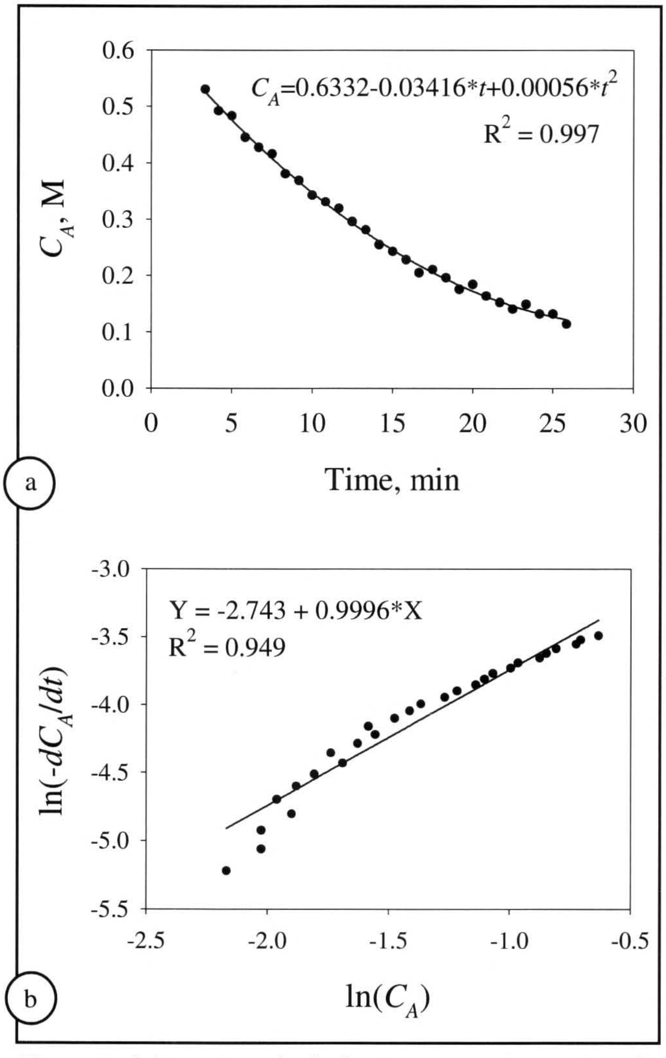

Figure 7. *(a) Acetic anhydride concentration vs. time for the batch reactor at 15°C fitted to a polynomial. (b) Differential method used to determine the reaction rate constant and order.*

sis. First, the concentration-time data are fitted to a polynomial, as shown in Figure 7a. The polynomial is differentiated to obtain the rate of reaction (dC_A/dt). As Eq. (10) illustrates, a plot of $\ell n(-dC_A/dt)$ vs. $\ell n(C_A)$ should give a slope equal to the reaction order and an intercept of $\ell n(k)$. Figure 7b represents a reaction with an order of one and a specific reaction rate of 0.0644 min^{-1}, which differs by 2% from the value obtained by the integral method and -20% from that reported in the literature,[4] which is 0.0806 min^{-1}.

Laboratory Period 3: Isothermal Semibatch Reactor

In this part of the experiment, the students use the rate expression obtained in the previous laboratory period to predict the concentration profile in an isothermal Semibatch reactor. The software "Polymath" is used to solve the differential equation given above (Eq. 11). In this experiment, the run is divided into two periods. In the first period, the Ac_2O is added to water at a particular rate. Subsequently, the addition of Ac_2O is stopped and the reaction proceeds in batch mode until all the Ac_2O is consumed. The experiments can be varied for different groups by changing the addition rate, the amount of Ac_2O added, or the reaction temperature. Figure 8 illustrates the simulated and experimental concentration profiles for a run carried out at 25°C where a total of 29 ml of acetic anhydride was added at an average rate of 3.55 ml/min. There is close agreement between the predicted and the experimental data, with a maximum difference of around 10% in the case of acetic acid at the end of the run and around 20% in the case of the acetic anhydride at the end of the addition. The slight discrepancy may be due to errors in the measurement of concentration of acetic acid, due to errors in the parameters of the rate expression, due to a slight deviation from isothermal operation because of heat of mixing and exothermic nature of the reaction, and/or due to errors in determination of the volumetric addition rate.

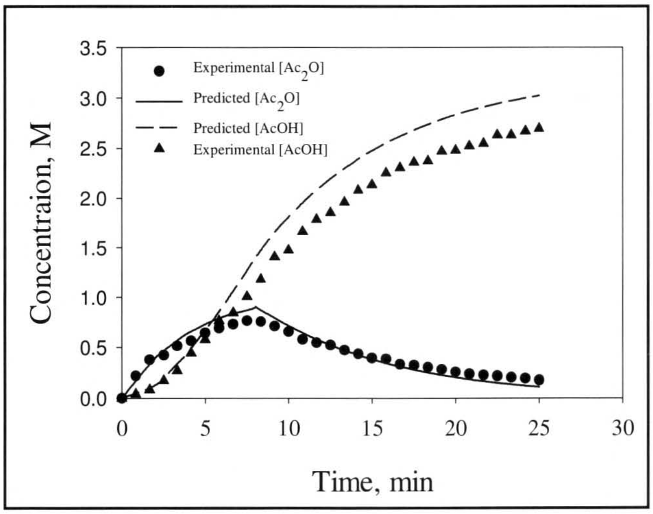

Figure 8. *Comparison between the predicted and experimental data obtained for an isothermal semibatch reactor at room temperature.*

CONCLUSIONS

The use of *in-situ* FTIR spectroscopy for following the hydrolysis of acetic anhydride reaction has been demonstrated. The analysis of the batch reactor 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 and were used to predict the performance of a semibatch reactor. Predicted acetic anhydride and acetic acid concentrations were in good agreement with the experimental concentrations. The undergraduate students found this laboratory experience a good opportunity to implement many of the concepts they learned in their reaction engineering course.

NOMENCLATURE

A	Arrhenius pre-exponential factor
C	concentration
C_A	acetic anhydride concentration
C_{A0}	initial or entering acetic anhydride concentration
C_B	water concentration
C_{B0}	initial water concentration
E	activation energy
k	reaction rate constant
k'	pseudo reaction rate constant
N	number of moles
n,m	reaction order
r	reaction rate
R	universal gas constant
t	time
T	temperature
V	volume
ν_0	volumetric flow rate

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