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# Kinetic Studies on Saponification of Ethyl Acetate Using an Innovative Conductivity-Monitoring Instrument with a Pulsating Sensor

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**ABSTRACT:** An innovative conductometric measurement technique using a nonconventional but high-performance (high-precision, high-resolution, rapid response features for online graphic display) in house-built pulsating conductivity monitoring instrument has been deployed to study the kinetic behavior during the reaction of ethyl acetate and NaOH. A laboratory-made constant temperature reaction bath with the facility of continuous stirring of solution for homogeneous mixing was used to carry out experiments at desired solution temperatures. Rate constants of the saponification reaction in the temperature range at various temperatures (30–55°C) were determined, and the results were compared with the reported values. Although the reported data exhibit wide scatter, our data are in agreement with some of the literature data. From these data, thermodynamic parameters such as activation energy, activation enthalpy, activation entropy, and activation free energy have been evaluated. With the introduction of this novel conductometric measurement technique, the determination of rate constants at various solution temperatures becomes much simpler and faster. © 2011 Wiley Periodicals, Inc. *Int J Chem Kinet* 1–9, 2011

## INTRODUCTION

In our laboratory, we have taken up a project to study the effect of temperature on oscillatory chemical reactions using our in house-built pulsating sensors. The

primary objective of this activity is to develop a suitable methodology to use the oscillatory reaction as a platform for rapid chemical assay. Before augmenting the pulsating sensor to study the kinetics of the oscillatory reaction, we preferred to study the kinetics of a well-known nonoscillatory reaction using a pulsating sensor to verify the reliability of our measurement technique for kinetic investigation of an unknown system. Hence, we chose one of the most popular

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reactions—the saponification reaction of ethyl acetate and sodium hydroxide—for the kinetic study.

The hydrolysis of ethyl acetate is one of the most well-known reactions in chemistry, and it is represented as a model example of the second-order reaction in the literature dealing with chemical kinetics [1,2]. This reaction has been studied by several investigators at different temperatures using a variety of measurement techniques [3–9]. Daniels et al. [3] and Smith and Levenson [4] adopted a volumetric titration method independently, in which the composition of reacting mixture was followed by an analysis of sample aliquots withdrawn from the reaction vessel at definite time intervals. The precision of the method is limited by the withdrawal of appropriate volume of sample at a fixed duration in addition to errors associated with titration using a color indicator. The second technique reported by Walker [5] depends on conductometric measurements to determine the composition at any given time. This conductometric technique avoids periodic withdrawal of samples for analysis. The measurements were carried out manually. However, the reliability of results fully depends upon the response time and reproducibility in a conductivity measurement. Another technique reported by Stead et al. [6] uses a continuous flow system, where the reactants are fed continuously at constant temperature into a stirred vessel. The method uses of a large volume of solution. Jensen et al. [7] used high-frequency titrimetry. The method does not need any external indicator or introduction of any electrodes into the reaction vessel. Although the authors have taken precaution to introduce a calibration technique for the nonlinearity of the instrument performance, it involves a number of manual operations in methodology as compared with the proposed method. Shui-yuan et al. and Ge-li et al. [10,11] used acidometry and microcalorimetry techniques, respectively, to determine rate constant of saponification of ester. However, these latest techniques are not as simple as the proposed technique. Zhanjun et al. [12] and Yong-Tao et al. [13] focused their attention on online data acquisition using a conductometric technique to make the methodology much simpler. However, the conventional conductivity sensors used by these authors are not as precise as the innovative sensors used in the present work.

Although various studies have been conducted by several investigators, there is significant scatter in data on the rate constant and activation energy in the saponification reaction of ethyl acetate and sodium hydroxide [4,7–9]. While augmenting our new measurement approach for such a study, we analyzed these results and independently determined the rate constant of this reaction and the related thermodynamic parameters fol-

lowing our own measurement technique. Moreover, there is always a need for continuous evolution of a simplified method for a kinetic study of any reaction in a more convenient way. A brief description of this unique approach of rapid online conductivity measurement using our in house-built pulsating sensor with special attention given to its use in the kinetic study and comparison of our results with the literature data reported by several investigators [4,7–9,14] are presented in this paper.

## PRINCIPLE OF CONDUCTIVITY MEASUREMENT

For the kinetic study using a conductometric measurement approach, a high-performance (high precision, high sensitivity, and very fast response) conductivity meter is the best choice. Fortunately, in our laboratory, such type of a conductivity-monitoring unit has already been developed and is used for many miscellaneous applications [15–18]. The working principle and the design of this conductivity meter are entirely different from the conventional conductivity monitoring instruments available in the market. The conductivity meter is designed in such a way that the conductivity cell forms a part of a specially designed logic gate oscillator (LGO) circuit. Once the cell is disconnected from the rest of the electronics, it will not act as an oscillator. This conductivity sensor is operated at 5 V DC with very low power consumption. When it is powered, the oscillator oscillates between two logic states (max: 1, min: 0). The output of the sensor is a train of rectangular pulses of 5-V amplitude from which the pulse frequency can be determined. The frequency of the LGO changes with the change in the ionic conductivity of the solution taken in the cell. This frequency is directly related to the conductivity of the solution. Prior to the deployment of a conductivity probe for a particular application, it is calibrated using a series of standard KCl solutions to establish a relationship between frequency and conductivity of solution following a multi-point calibration technique developed in-house. From the calibration plot, a polynomial equation (either in second degree or in third degree) is generated, the coefficients of which are loaded in the software to give a direct display of conductivity during measurement. In the present case, the instrument is designed in such a way that with a change in the conductivity of the solution by  $1 \mu\text{S cm}^{-1}$ , there is a change of about 20 Hz in pulse frequency. Even in some specific applications such as online radiation dosimetry, assay of boron in heavy water, and assay of the heavy water content in a mixture of light water and heavy water,

where it was required to monitor a very minor shift in the conductivity, were addressed by using our pulsating conductivity monitoring technique with minor modification in the design of probes and associated electronics [18]. Because of these advantages, in the present work we applied this new type of the conductivity monitoring device (response time:  $<1$  s, resolution:  $0.1 \mu\text{S cm}^{-1}$ , relative standard deviation [RSD]: 0.5%) in the kinetic study.

## EXPERIMENTAL

### Chemicals

All chemicals used for this work are of AR grade. The stock solutions of NaOH ( $\sim 1$  M) and glacial acetic acid ( $\sim 1$  M) were prepared using high-purity distilled water (Millipore water conductivity less than  $1 \mu\text{S cm}^{-1}$ ), whereas ethyl acetate (Fisher Scientific, Mumbai, India; Qualigen, Mumbai, India; density:  $0.898 \text{ g cm}^{-3}$ ) was directly used as stock solution. Stock solution of NaOH was standardized against freshly prepared standard oxalic acid. All working standards used in this work were freshly prepared before continuing the experimental campaign.

### Conductivity Monitoring Instrument

A pulsating sensor based conductivity monitoring instrument [19] was used in the present study. A vertical-type Teflon probe with a pair of platinum electrodes (platinum rods with 0.5 mm diameter, 5 mm length, 5 mm gap between electrodes) fixed onto the bottom of it was used for online monitoring of conductivity shift during kinetic experiments. The conductivity probe was connected to the associated electronics of LGO. The LGO was connected to a personal computer (PC) via a power supply cum signal routing unit. In this case, a fixed capacitor is used in the LGO, whereas the conductivity cell forms the resistivity part of the oscillator circuit. When the LGO is operated by 5 V DC, a train of rectangular pulses are generated from which the pulse frequency is determined. The train of pulses is sent directly to the PC through its parallel port. The in house-developed software package converts pulses to frequency and then from frequency to the respective conductivity. The frequency value purely depends on conductivity of solution for a fixed LGO circuit. Even for a fixed conductivity value, the frequency can be altered by changing the capacitance part of the timing oscillator. While doing so, one has to consider regarding stability and uncertainty in measurement. Accordingly the appropriate oscillator circuit can be designed for

specific applications. The advantage of adopting this innovative conductivity measurement technique is that the primary signal from the sensor end is in a direct digital form, i.e., the output is digital pulse frequency. Hence, it avoids additional instrumentation for analog-to-digital conversion unlike conventional instrumentation. Since the primary signal is in a digital domain form, the signal loss during long distance transmission is practically nil and it possesses excellent noise immunity. In the present application, the frequency varies from 50 to 6255 Hz, which covers the conductivity range from  $\leq 1$  to  $1000 \mu\text{S cm}^{-1}$ . In this kinetic study, the pulse counting is done at every 1-s interval. Using our indigenously made data acquisition system, the online data in graphic form are recorded and stored for future use. The detailed instrumentation, calibration technique, and the performance of this innovative conductivity meter have been described in one of our latest publications [19].

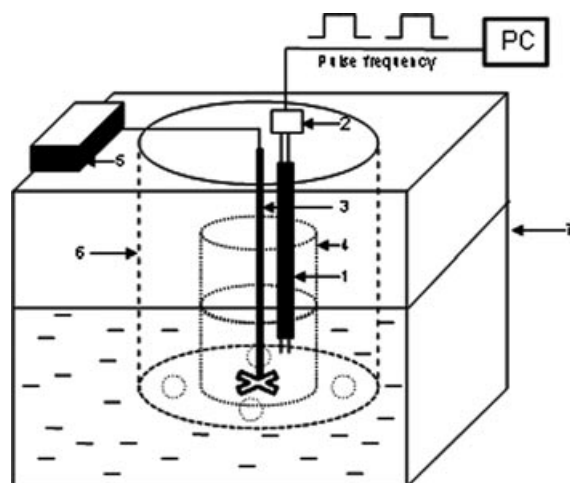
### Experimental Setup

Initial kinetic studies were conducted at room temperature to determine the order of the reaction in saponification of ester. A fixed volume of desired solution was taken in a beaker in which the conductivity probe was mounted vertically. A commercially available magnetic stirrer was used to mix the solution homogeneously. A series of experiments were conducted at prevailing solution temperature to determine the order of the reaction.

Further experiments were carried out at desired solution temperatures with the goal of determining the rate constant of the reaction at different temperatures. An experimental facility was designed and made in our laboratory to carry out the experiments at a fixed solution temperature. A high-precision constant temperature bath (Siskin Julabo VPC, which could maintain temperature of  $\pm 0.1^\circ\text{C}$ ) was used for this application. A microcontroller-based vertical-type stirrer using a dc stepper motor was made in-house. Arrangement was made to mount a beaker holder in the temperature bath. The reaction vessel containing solution was placed inside it. The vertical stirrer was fixed in the reaction vessel to mix the solution homogeneously throughout the experiment. The conductivity probe was also vertically placed in the solution to monitor the conductivity of solution during the experiment. Figure 1 shows a schematic diagram of experimental setup.

### Methodology

Twenty-five milliliter of distilled water was taken in the reaction vessel and kept in the constant



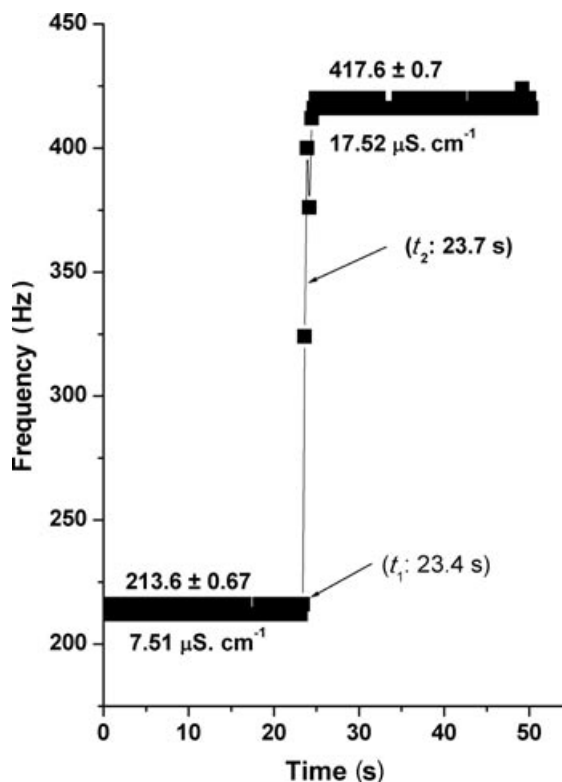
**Figure 1** Experimental setup for the kinetic study (1: conductivity probe; 2: logic gate oscillator; 3: vertical stirrer; 4: reaction vessel; 5: speed control unit; 6: reaction vessel holder; and 7: temperature bath).

temperature bath. After attaining a desired solution temperature, 0.5 mL of 0.1 M NaOH and 0.5 mL of 0.1 M ethyl acetate (both reactants were maintained at same the temperature prior to their addition) were added to it and immediately real-time conductivity of solution was monitored for a fixed duration (500–1000 s) at every 1-s interval using our PC-based conductivity monitoring unit. Immediately after the experiment, the data acquisition can be terminated and saved for further off-line processing.

To measure the conductivity of the solution at infinite time, instead of continuing this experiment for a long period, a new approach was adopted. Twenty-five milliliters of distilled water was taken in a beaker at a constant temperature, and after attaining the temperature 0.5 mL of 0.1 M acetic acid and 0.5 mL of 0.1 M NaOH were added to it. Thus sodium acetate, which was formed as the product in the above reaction, attributed for the conductivity at infinite time ( $\kappa_{\infty}$  at constant temperature).

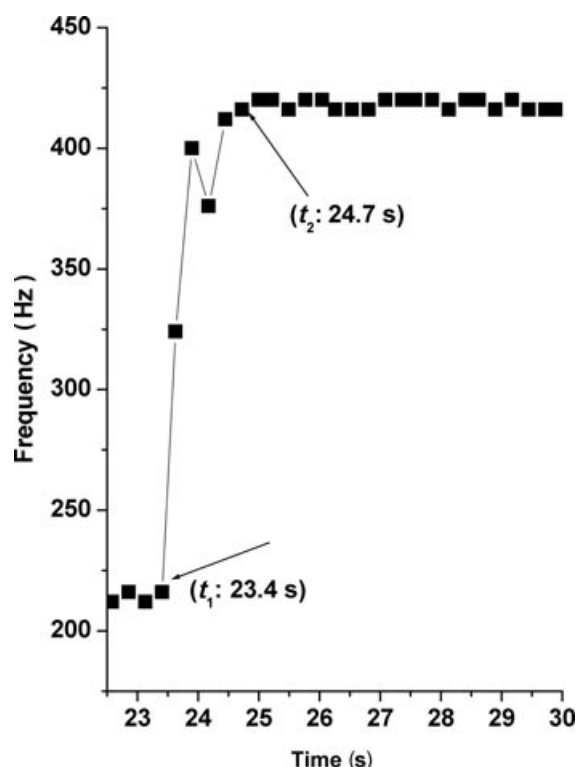
## RESULTS AND DISCUSSION

At the outset, we investigated the potential of our pulsating conductivity meter to assess its suitability for a rapid kinetic measurement. Hence, we conducted appropriate experiments to determine the response time, precision in measurement, and influence of reagent mixing time on measurement. Figure 2 shows that with the addition of 100  $\mu\text{L}$  of 0.01 M KCl solution to 25 mL of dilute KCl solution with a fixed conductivity, the pulse frequency shifts from 7.5 to 17.5  $\mu\text{S cm}^{-1}$ .



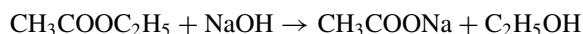
**Figure 2** Demonstration of response time of the pulsating-type conductivity-monitoring instrument ( $t_1$ : time in seconds when the reagent was added;  $t_2$ : time in seconds corresponding to 63% of an increase in signal).

This shows that the shift in frequency per change in the conductivity of 1  $\mu\text{S cm}^{-1}$  is about 20 Hz. The precision in measurement is less than 0.7 Hz, and the resolution of instrument used for the present application is about 0.1  $\mu\text{S cm}^{-1}$ . However, resolution can be further improved by slightly modifying the geometry of electrodes and the capacitive component of instrumentation [19]. The response time, which is defined as the time required by the instrument to respond 63% of a sudden change in signal, has been evaluated from this figure. In this figure, the presence of a small shoulder, which gives an apparent impression of noise level, is not the noise level, but it is due to the actual phenomenon of conductivity shift during the mixing of reagents before attaining the stable homogeneous value. This phenomenon is demonstrated in Fig. 3, which is derived from Fig. 2. The time corresponding to the reagent addition and the time corresponding to the stable conductivity value achieved after homogeneous mixing are clearly indicated in this figure. From this, it is clearly realized that the time of mixing to get a homogeneous solution is about 1.3 s, which includes the time required for addition of reagent.

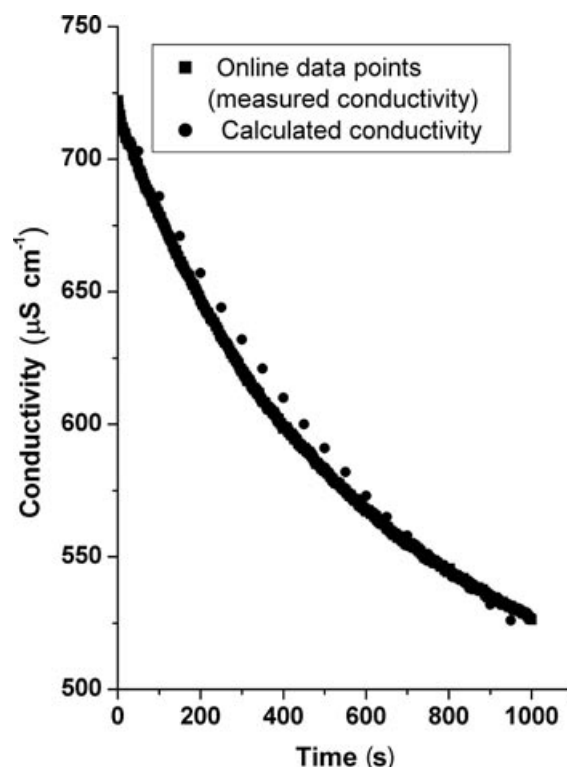


**Figure 3** Demonstration of kinetics of mixing of reagents ( $t_1$ : time in seconds when the reagent was added;  $t_2$ : time in seconds corresponding to the steady value after homogeneous mixing).

It is well known from the literature that the saponification of ethyl acetate in the presence of a strong base (NaOH) is a second-order reaction, in which both the reactants are consumed to form sodium acetate and ethyl alcohol.



In the present work, the concentration of each reactant in the bath has been taken as equimolar to avoid the system to turn into an exponential decay after a long time. With the progress of the reaction, highly conducting  $\text{OH}^-$  ions (equivalent ionic conductance,  $\lambda_{\text{OH}^-}^0$ : 199.2  $\text{S cm}^2 \text{equiv}^{-1}$  [20]) in the solution were replaced by an identical number of less conducting acetate ions ( $\lambda_{\text{CH}_3\text{COO}^-}^0$ : 41  $\text{S cm}^2 \text{equiv}^{-1}$  [20]), resulting in a continuous decrease in conductivity of solution. From the onset of reaction, the decrease in conductivity was continuously monitored online using a high-performance laboratory-made pulsating conductivity meter. Figure 4 shows an online graphic view of conductivity with respect to time during the saponification reaction conducted at a constant temperature. Such a smooth online plot was generated due to fast



**Figure 4** Real-time plot of conductivity versus time for the saponification reaction at a constant solution temperature ( $323.0 \pm 0.1 \text{ K}$ ).

response and high precision in measurement using a pulsating conductivity sensor. The conductivity of solution during the reaction at every 1-s interval is shown on the online plot. From this online plot using a cursor navigation, conductivity values of solution at each 100-s interval were extracted and are presented in Table I. In each case, conductivity contributed by distilled water was deducted and corrected conductivity values were tabulated. To determine the specific conductance at infinite time instead of continuing measurement for a prolonged period as used conventionally, we adopted a new approach. At infinite time, both reactants, ethyl acetate and NaOH, are completely converted to sodium acetate and ethyl alcohol as the reaction product. The conductivity of solution in the reaction vessel is governed by sodium acetate since ethyl alcohol will not contribute to conductivity change. Hence, the conductivity of a synthetic sodium acetate solution (prepared by using NaOH and acetic acid of equimolar concentration, 1.92 mM) corresponding to same molar concentration of either of the reactant (1.92 mM in this case) refers to the conductivity at infinite time. Thus, this approach avoids having to carry out measurement for a prolonged period (at least for 2 h). From these data, as given in Table I, the rate constant at

**Table I** Data for the Computation of Rate Constant in the Saponification Reaction at a Constant Temperature

Time, $t$ (s)	Specific Conductance, $\kappa_{\text{soln.}}$ ( $\mu\text{S/cm}$ )	Specific Conductance (Corrected), $\kappa_t$ ( $\mu\text{S/cm}$ )	$(\kappa_0 - \kappa_t) = A$	$(\kappa_t - \kappa_\infty) = B$	$A/B$
0	721.6	720.2	0	438.1	0
100.3	678.9	677.5	42.7	395.4	0.11
200.7	646.9	645.5	74.7	363.4	0.21
300.2	619.8	618.4	101.8	336.3	0.30
400.5	599.4	598.0	122.2	315.9	0.39
500.9	582.5	581.1	139.1	299.0	0.47
600.4	567.8	566.4	153.8	284.3	0.54
700.7	554.9	553.5	166.7	271.4	0.61
800.2	545.2	543.8	176.4	261.7	0.67
900.6	535.4	534.0	186.2	251.9	0.74
1001	526.1	524.7	195.5	242.6	0.81

Composition of bath solution:  $[\text{ethyl acetate}]_0 = 1.92\text{e-}3 \text{ M}$ ;  $[\text{NaOH}]_0 = 1.92\text{e-}3 \text{ M}$ .

Bath temperature: 323 K.

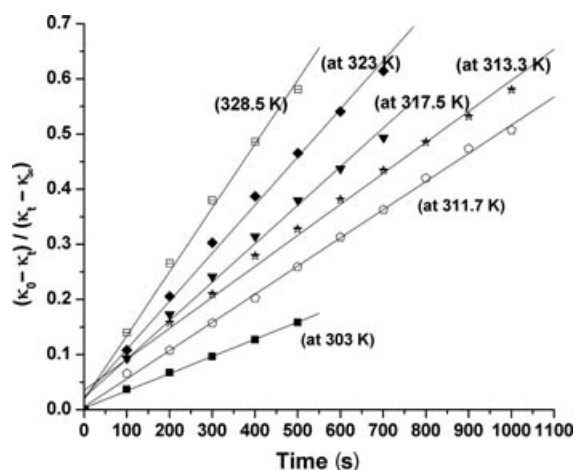
Specific conductance of distilled water at solution temp:  $1.40 \text{ S cm}^{-1}$ .

$\kappa_t$ : specific conductance of solution at  $t$ ,  $\text{S cm}^{-1} = (\kappa_{\text{soln.}} - 1.40)$ .

$\kappa_0$ : specific conductance at  $t = 0$  (here  $\kappa_0 = 721.6 - 1.4 = 720.2 \text{ (S cm}^{-1})$ ).

$\kappa_\infty$  = specific conductance at  $t = \infty$ . ( $\kappa_\infty = 283.5 - 1.4 = 282.1 \text{ (S cm}^{-1})$ ).

a constant solution temperature was determined using the relation cited in the literature [21,22]. We also verified this real-time conductivity plot with the calculated conductivity values using the rate constant at this temperature determined in the present work. To do so, we used the initial concentration of reagents, initial solution conductivity, conductivity at infinite time as used in this experimental run as the input parameters. The data points corresponding to the calculated conductivity values at every 50-s interval are placed in the experimental plot. Both experimental and calculated values agreed well.



**Figure 5** Plot of  $(\kappa_0 - \kappa_t) / (\kappa_t - \kappa_\infty)$  against time for the determination of rate constants of the reaction at different solution temperatures.  $[\text{EtAc}]_0$ : 1.923 mM;  $[\text{NaOH}]_0$ : 1.923 mM.

Figure 5 shows the plots of  $(\kappa_0 - \kappa_t) / (\kappa_t - \kappa_\infty)$  at different solution temperatures in a typical experimental campaign. The slope of each plot was used for the determination of the rate constant. It is observed that in some cases the plots show the presence of intercepts (about 0.03–0.035) instead of showing zero, as predicted theoretically. The presence of such small intercepts is attributed possibly to difficulty in exact determination of the  $\kappa_0$  value at elevated temperature. Since the saponification reaction is a relatively fast reaction, and the reaction becomes still faster at elevated temperature, it might have been difficult to detect the exact conductivity of solution before the onset of the reaction even if a number of precautions have been taken for faster addition of reactant, counting time, rapid homogeneous mixing, and a uniform stirring rate, etc. The presence of such a small value of intercept was not observed in two experiments conducted at relatively lower temperature. Moreover, as we are able to get highly reliable data in conductivity during the reaction, data acquisition for a period of 500 s will be sufficient to get information about the rate constant. Thus, the proposed technique is quite faster than the other measurement techniques reported by earlier investigators.

To ensure the reliability in the determination of rate constants at different constant solution temperatures, we conducted seven measurement campaigns at each solution temperature. The rate constant at each temperature computed from the respective slope is presented in Table II. The uncertainty in the determination of slopes from seven independent measurements and the

**Table II** Rate Constants of the Saponification Reaction at Different Temperatures

Temperature, $T$ (K)	Slope <sup>a</sup>	Rate Constant, $k^a$ (L mol <sup>-1</sup> s <sup>-1</sup> )
303	$3.11\text{e-}04 \pm 2.80\text{e-}06$	$1.62\text{e-}01$ (%RSD: 0.9)
311.7	$5.11\text{e-}04 \pm 5.62\text{e-}06$	$2.66\text{e-}01$ (%RSD: 1.1)
313.3	$5.38\text{e-}04 \pm 5.16\text{e-}06$	$2.80\text{e-}01$ (%RSD: 0.96)
317.5	$6.66\text{e-}04 \pm 5.86\text{e-}06$	$3.46\text{e-}01$ (%RSD: 0.88)
323	$8.40\text{e-}04 \pm 9.41\text{e-}06$	$4.37\text{e-}01$ (%RSD: 1.12)
328.5	$1.16\text{e-}03 \pm 1.28\text{e-}05$	$6.03\text{e-}01$ (%RSD: 1.1)

<sup>a</sup>Precision in measurement is calculated based on seven independent experimental results.

uncertainty in the determination of rate constants are also indicated in this table. Results from the above experimental campaigns show excellent agreement. Using these data for rate constants at different temperatures, the activation energy was determined and is presented in Table III. The other thermodynamic parameters in the saponification reaction of ethyl acetate and sodium hydroxide such as activation enthalpy, activation entropy, and free energy of activation were computed using the data for rate constants at different temperatures following the Eyring equation [22], and they are shown in Table III. In the Eyring equation,  $\Delta C_p^\ddagger$  is considered to be very small and the reaction is considered to be 100% completion. It shows excellent agreement in these thermodynamic parameters with RSD varying from 0.9% to 1.4%.

The rate constant at 30°C and activation energy for the saponification reaction, as obtained from the present work, were compared with the data reported by earlier investigators in Table IV. This table shows significant scatter in the data for both the reaction rate and activation energy reported [4,7–9,14]. In the present work, the rate constant at 30°C is 0.16 L mol<sup>-1</sup> s. It is in agreement with the values reported by Tsujikawa

et al. [8], Jensen et al. [7], and Warder [14]. The value reported by Smith et al. [4] is about 30% lower than our value. They also reported a very high value of activation energy (61.4 kJ mol<sup>-1</sup>) [4] with respect to the value reported in this work. Such a large deviation in the values on the rate constant as well as activation energy can be attributed to errors associated with a volumetric titration technique by withdrawal of aliquots of the sample at a periodic interval (off-line techniques).

Recently, Schneider and Stoessel [9] used the commercial microcalorimeter integrated with a microreactor for kinetic investigation in the flowing system. In their study, they used 0.8 M ethyl acetate and 1.0 M NaOH and conducted the experiments at five different temperatures ranging from 30 to 70°C. They obtained the value of activation energy, 46.5 kJ mole<sup>-1</sup>, which was about 10% higher than the present value. The authors have taken a number of precautions, such as (i) good mass transfer using a small radius of microchannel, (ii) homogeneous mixing of reactants by designing the microreactor as a plug-flow reactor for a continuous operation at steady state, and (iii) selection of a calorimeter with high thermal sensitivity to carry out the experiment. The measurement is based on the heat

**Table III** Thermodynamic Parameters in Saponification Reaction

Serial Number of Experimental Campaign	Activation Energy (kJ mol <sup>-1</sup> )	Activation Enthalpy (kJ mol <sup>-1</sup> )	Activation Entropy (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G(298\text{ K})$ (kJ mol <sup>-1</sup> )
1	42.1	39.1	-131.1	78.2
2	40.7	38.1	-128.5	76.4
3	41.5	38.1	-133.2	77.8
4	40.8	38.2	-131.3	77.3
5	41.8	39.1	-130.9	78.2
6	41.2	38.5	-131.9	77.8
7	42.0	39.3	-130.3	78.2

Activation energy:  $41.4 \pm 0.6$  kJ mol<sup>-1</sup>.

Activation enthalpy:  $38.6 \pm 0.5$  kJ mol<sup>-1</sup>.

Activation entropy:  $-131.0 \pm 1.4$  J mol<sup>-1</sup> K<sup>-1</sup>.

Free energy of activation (298 K):  $77.7 \pm 0.7$  kJ mol<sup>-1</sup>.



**Table IV** Comparison of Results

Investigators	Rate Constants at 30°C (L mol <sup>-1</sup> s)	Activation Energy (kJ mol <sup>-1</sup> )	Technique Adopted
Smith et al. [4]	0.11	61.4	Volumetric titration
Jensen et al. [7]	0.15	–	High-frequency titrimetry
Tsujikawa et al. [8]	0.16 <sup>a</sup>	48.4	Conductivity measurement
Schneider and Stoessel [9]	0.19 <sup>a</sup>	46.1	Microcalorimetry
Warder [14]	0.14	–	–
Present work	0.16	41.4	Pulsating conductivity sensor

<sup>a</sup>Data computed from the corresponding plots available in the literature.

changes during the reaction. In our work, the direct online conductivity measurement of solution immediately after the onset of reaction is recorded, which provides kinetic information of the entire process. In view of simplicity in instrumentation and measurement technique, the conductivity approach using the pulsating sensor seems to be a better approach for the kinetic study. Our reported value on activation energy is about 10% lower than the values reported by Tsujikawa et al. and Schneider and Stoessel, as shown in Table IV.

The values for activation energy and other related thermodynamic parameters are based on seven independent campaigns carried out in this laboratory using the pulsating sensor, which show an excellent agreement. This was possible due to augmentation of a high-performance pulsating conductivity monitoring system along with the in house–built experimental facility specially designed for carrying out the kinetic study at a desired temperature. The high precision in conductivity measurement of extremely dilute solution using this innovative approach could permit us to carry out all kinetic experiments successfully using reactants at a millimolar concentration level. Fast response and rapid online measurement with the pulsating sensor made it possible to complete an experimental campaign for the measurement of the rate constant within a short duration (even in 500 s). This minimized the error associated with CO<sub>2</sub> pickup from atmosphere by NaOH and evaporation loss of ethyl acetate during the experiment.

## CONCLUSION

Pulsating sensors developed at the Innovative Instrumentation Section (of the Electronics and Instrumentation Group) have already been deployed in many miscellaneous laboratory and field applications. With this new approach of conductivity measurement, it was possible to demonstrate the determination of the rate constant of a well-known system at different temperatures with high degree of precision in a much simpler way. This precise determination of the rate constant

led us to evaluate thermodynamic parameters for the saponification reaction. The values are in good agreement with the recent data based on the microcalorimetric technique. It will be extremely useful for researchers and the students to use this novel measurement technique for the kinetic study in any other system, which needs a precise measurement of conductivity.

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