Research Article

Kinetic Studies on Saponification of Poly(ethylene terephthalate) Waste Powder Using Conductivity Measurements

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Conductometric measurement technique has been deployed to study the kinetic behavior during the reaction of poly(ethylene terepthalate) (PET) and NaOH. A laboratory made arrangement with facility of continuous stirring was used to carry out experiments at desired temperature. With conductometry, the determination of kinetic as well as thermodynamic parameters becomes more simple and faster as compared to gravimetry. Chemical kinetics of this reaction shows that it is a second order reaction with reaction rate constant $2.88 \times 10^{-3} \, \text{g}^{-1} \, \text{s}^{-1}$ at 70°C. The specific reaction rates of the saponification reaction in the temperature range at various temperatures (50–80°C) were determined. From the data, thermodynamic parameters such as activation energy, Arrhenius constant (frequency factor), activation enthalpy, activation entropy, and free energy of activation obtained were $54.2 \, \text{KJ} \, \text{g}^{-1}$, $5.0 \times 10^{6} \, \text{min}^{-1}$, $90.8 \, \text{KJ} \, \text{g}^{-1}$, $-126.5 \, \text{JK}^{-1} \, \text{g}^{-1}$, and $49.9 \, \text{KJ} \, \text{g}^{-1}$, respectively.

1. Introduction

The saponification of poly(ethylene terephthalate) (PET) is one of the known reactions in polymer chemistry and it is represented as an example of pseudofirst order in the literature dealing with chemical kinetics [1, 2]. This reaction has been studied by several investigators at different temperatures using different techniques and reagents. Alcoholysis has been carried out by different workers [3–9]. Hydrolysis of PET gives terephthalic acid (TPA) and ethylene glycol (EG) as a reaction product [10–13]. Aminolysis and methanolysis [14–16] give dimethyl terephthalate (DMT) and terephthalamide as a reaction product. Acid alkali and water hydrolysis of PET waste in organic solvent have been reported by several workers [17–21].

Kinetics of a phase transfer catalyzed alkaline hydrolysis of PET has been studied by Kosmidis et al. [22, 23]. They have used trioctylmethylammonium bromide as phase transfer catalyst. The method is useful because,

nowadays, terephthalic acid is replacing dimethyl terephthalate as the main monomer in the industrial production of PET. Chemical recycling of PET has been carried out by Karayannidis and Achilias [24]. They found an effective way for production of secondary value-added materials.

Alkaline hydrolysis of PET belongs to relatively frequently investigated reactions. Most often, the course of reaction is studied by gravimetry in withdrawn samples. The error in the kinetic and thermodynamic parameters are more in gravimetry as compared to conductometry. Another disadvantage of this method is high Inplace of labouriosity change time and considerable consumption of chemicals.

Hence, in the present work, an online conductivity measurement is carried out to evaluate the second order reaction rate constants with possibly lowest experimental error for saponification of PET waste powder in order to obtain information about activation energy, activation enthalpy, activation entropy, and free energy of activation.
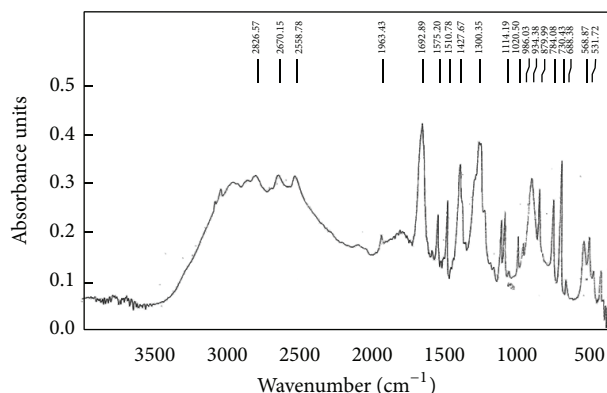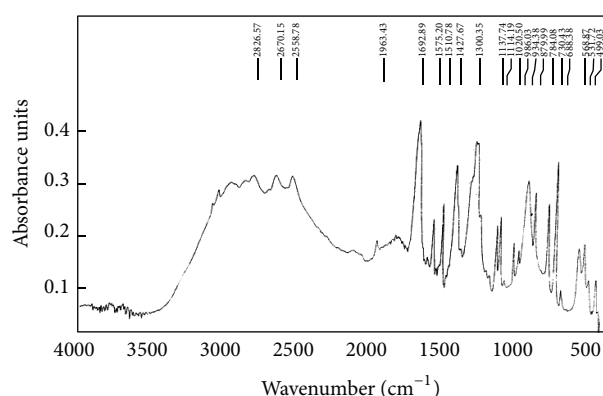
FIGURE 1: FTIR spectrum of pure TPA.

FIGURE 2: FTIR spectrum of TPA obtained by conversion of PET waste powder.

2. Experiment

All chemicals used in the present work were of analytical reagent grade. The solution of NaOH was prepared using conductivity water. PET waste bottles were procured from local corporation area of Nagpur, Maharashtra state, India. The bottles were dipped into the solution of Teepol and then washed using double distilled water. Finally, washed with high-purity water having Millipore water conductivity less than $1 \mu s \, cm^{-1}$. All the bottles were dried with hot air blower. The cleaned and dried bottles were chilled to increase their brittleness, then, crushed, ground, and sieved into different particle sizes ranging from 800 to 100 μm.

The optimum parameters for saponification of PET waste powder were determined by gravimetric measurements. PET waste powder (2–12 g) was taken into 100 mL of conductivity water containing (4–10 g) of sodium hydroxide, and 3 mL of pyridine was added to keep the reaction mixture at pH 14. The reaction mixture was refluxed at 50–80°C for 150 minutes in 250 mL three-vertical-neck round bottom flask equipped with a reflux water condenser, microcontroller based stirrer, and internal digital temperature measurement probe. After 150 min, the cooled reaction mixture was filtered to separate

PET powder residue and sodium salt of TPA. The salt was precipitated with stoichiometric amount of HCl. A white precipitate of TPA, after complete removal of chloride ions, was vacuum dried at 90°C for 2 h. The product obtained by saponification was characterized by instrumental analysis such as FTIR spectra (Figure 1). FTIR spectra of product were compared to standard TPA spectra (Figure 2). The optimum parameters determined were further used for the kinetic measurement using conductometry.

In kinetic measurements, three-vertical-neck round bottom flask was fixed with refluxed water condenser, an internal digital temperature measurement probe, a conductivity measuring cell, and microcontroller based vertical type of stirrer. The conductivity cell used was a vertical Teflon probe with platinum electrodes. The cell constant of the cell was about unity. It was cleaned with hydrochloric acid solution and ensured its platinized layer of platinum black before being used. The cell was treated with water or reaction mixture in which PET waste was saponified to give similar concentrations of ions as in the kinetic measurements. A conductivity measurement was made by using a digital conductivity meter made up of Equiptronic India Ltd. Since the aim of the work is to determine kinetic and thermodynamic parameters, the temperature stability and its measurement are important. High precision thermostat and digital temperature measurement probe were used in the present work (Figure 3).

Kinetic experiments were carried out at optimum parameters to determine the rate constant. 10 g PET waste powder (100 μm) and 3 mL of pyridine were added into the reaction flask placed in thermostat. Here, pyridine does not play any role in the kinetics. It maintains the reaction mixture at pH 14. The platinized electrode surfaces of the conductivity measuring cell and tip of the temperature probe were adjusted so that they are not struck by the vertical stirrer bar (Figure 3). 7 g sodium hydroxide in 100 mL conductivity water was placed in the separate 250 mL beaker in the thermostat to the desired reaction temperature. When the thermal equilibrium has been reached, sodium hydroxide solution was added to PET waste powder containing pyridine. Immediately, stopwatch was started. Online conductance of the reaction mixture was measured at various time intervals up to 150 min. C_w is the conductance of conductivity water and C_o, C_t, and C_∞ are the conductance of reaction mixture at times zero, t, and infinity, respectively. From these, the values of $C_o - C_t$ and $C_t - C_\infty$ were determined then $x \, \alpha \, (C_o - C_t)$ and $a - x \, \alpha \, (C_t - C_\infty)$. Where x is the amount of PET depolymerized at zero time, $a - x$ is the amount of PET depolymerized at time "t" and "a" is the initial amount of PET. Therefore for second order reaction if plot $C_o - C_t / C_t - C_\infty$ values (ordinate) against time t, is a straight line, rate constant can be deduced from the slope.

The order of reaction was determined by varying the amount of sodium hydroxide and PET waste powder in the reaction mixture. In both cases, rate constant was determined.

In order to evaluate kinetic and thermodynamic parameters, rate constant determinations were also carried out at various temperatures ranging from 50°C to 80°C. From
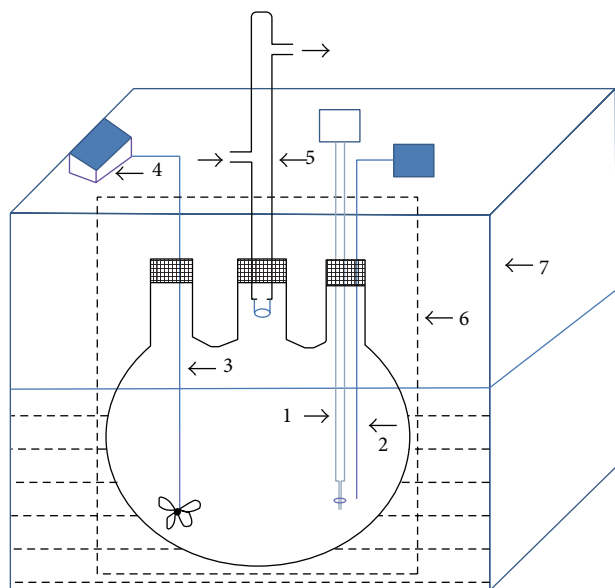
FIGURE 3: Experimental setup ((1) conductivity cell, (2) temperature sensor, (3) stirrer, (4) stirrer controller, (5) water condenser, (6) three-neck round bottom flask holder, and (7) thermostat).

TABLE 1: Optimum parameters for saponification.

Sr. number	Parameter	Optimum value by gravimetry
1	Particle size	100 μm
2	Amount of PET waste powder	10 g
3	Amount of NaOH	7 g
4	Temperature	70°C

$$\cdots [C(O)-C_6H_4-C(O)-O-CH_2-CH_2-O]_n \cdots$$
(PET waste powder)

NaOH/H$_2$O

$$NaO-C(O)-C_6H_4-C(O)-ONa \xrightarrow{HCL} HO-C(O)-C_6H_4-C(O)-OH$$
(sodium terephthalate)   (terephthalic acid)

+

$$HO-CH_2-CH_2-OH$$
(ethylene glycol)

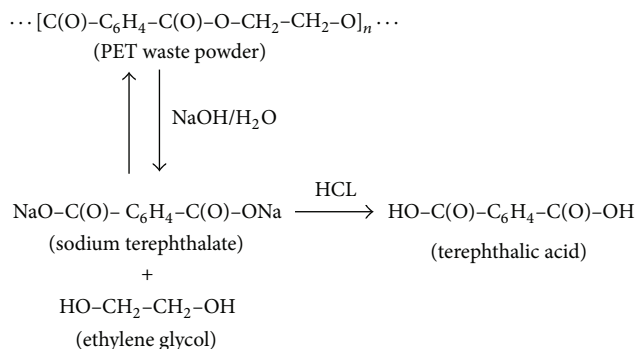SCHEME 1: Saponification of PET waste powder.

3. Results and Discussion

Saponification of PET waste powder was carried out using various amounts of PET waste powder, sodium hydroxide, and particle size. The saponification was also studied at different temperatures. The results of the optimum saponification parameters are shown in Table 1. These parameters are used to study the kinetics. Conductometric kinetics of saponification of PET waste powder was undertaken on the basis of the hydroxide ion and terephthalate formed in the reaction product. The reaction product was analyzed by FTIR spectra. The FTIR spectra of pure TPA and TPA obtained by saponification reaction were recorded. The FTIR in Figures 1 and 2 shows that the product obtained from saponification of PET waste powder has the same characteristic peaks as pure TPA. The peaks corresponding to aromatic rings are at wave numbers of 700 cm^{-1} and 800 cm^{-1}, while the peaks corresponding to carboxylic groups are at wave numbers 1730–1650 cm^{-1}. The peak at 3540 cm^{-1} is for hydroxyl end group and the peak at 3200 cm^{-1} is for carbonyl overtone. This suggests that the obtained product is TPA because its spectra are similar to those of pure TPA.

The rate constant of saponification was determined by online conductivity measurements at various time intervals. With progress of reaction, highly conducting OH$^-$ ions in the reaction mixture were replaced by an identical number of very less conducting terepthalate ions, resulting in continuous decrease in conductivity of the reaction mixture. From the start of the reaction, the decrease in conductivity was continuously monitored online using conductivity meter. The conductivity values at each 25 min. interval of time were recorded. In each case, conductivity contributed by conductivity water (C_w) was deducted and corrected conductivity values were recorded. At infinity time, both reactants, PET and NaOH, are completely converted to sodium terephthalate and ethylene glycol as a reaction product. Hence, the specific conductance at infinity time (C_∞) was recorded by measuring conductivity of reaction product after prolonged period of six hours. The conductivity of the product in the reaction vessel is governed only by sodium terephthalate since ethylene glycol does not contribute to conductivity change (Scheme 1). As shown in Scheme 1, each chain breaking utilizes two sodium hydroxide molecules to form one each of sodium terephthalate and ethylene glycol. Therefore, the progress of the reaction was studied by measuring the conductivity of the sodium hydroxide over a definite reaction time.

The specific conductivity of reaction mixture before the start of reaction, that is, at zero time (C_o), and at various reaction times (C_t) during the course of reaction was measured. The specific conductivity of conductivity water (C_w) was deducted from the specific conductivity at zero time (C_o) and from various reaction times (C_t) to get corrected values of C_o and C_t. With the help of corrected values of C_o and C_t, the values of $C_o - C_t$ were calculated. The values of $C_t - C_\infty$ were obtained by deducting the conductivity at infinity time (C_∞). From these values of $C_o - C_t$ and $C_t - C_\infty$ at various reaction times, the values of $C_o - C_t/C_t - C_\infty$ were evaluated (Table 2). A plot of $C_o - C_t/C_t - C_\infty$ shows a straight line passing through origin and indicates the second order kinetics (Figure 4). The slope of this plot gives the reaction rate constant. The reaction rate constant is 2.88×10^{-3} g^{-1}s^{-1} at 70°C. The reaction rate constant was determined by varying the PET waste powder (in grams) and NaOH (in grams).

TABLE 2: Reaction rate constant of saponification of PET waste powder.

Amount of PET waste powder: 10.0 g
Amount of sodium hydroxide: 7.0 g
Volume of pyridine: 3.0 cm^3
Temperature: 70.0°C
Specific conductance of conductivity water (C_w): 1.45 μs/cm
Specific conductivity of solution, C_0: 668.1 μs/cm
Specific conductivity at infinity, C_∞: 180.3 μs/cm

Time t/min	Specific conductance of reaction mixture μs/cm	Specific conductance of reaction mixture (corrected) μs/cm	$C_0 - C_t$	$C_t - C_\infty$	$\dfrac{C_0 - C_t}{C_t - C_\infty}$
00	C_0 = 668.1	C_0 = 666.6	—	—	—
25	C_t = 631.9	C_t = 630.5	36.1	450.2	0.08
50	C_t = 604.1	C_t = 602.6	64.0	422.3	0.15
75	C_t = 580.8	C_t = 579.4	87.2	399.1	0.22
100	C_t = 556.8	C_t = 555.4	111.2	375.1	0.30
125	C_t = 536.7	C_t = 535.3	131.3	355.0	0.37
150	C_t = 519.8	C_t = 518.4	148.2	338.1	0.44

Slope of the graph of $(C_0 - C_t)/C_t - C_\infty$ versus time = reaction rate constant, $k_2 = 2.88 \times 10^{-3}$ g^{-1}s^{-1}.

TABLE 3: Effect of temperature on saponification.

Amount of PET waste powder: 10.0 g
Amount of sodium hydroxide: 7.0 g
Volume of pyridine: 3.0 cm^3

Temperature t/°C	Temperature T/K	$1/T/10^{-3}$ K^{-1}	Reaction rate constant, $k_2/10^{-3}$ g^{-1}s^{-1}	$\log k_2$
50	323	3.10	0.88	−3.05
60	333	3.00	1.68	−2.77
70	343	2.92	2.88	−2.54
80	353	2.83	5.12	−2.29

Slope of the graph of $\log k_2$ verses $1/T$ = −2829 K.
Activation energy: E_a = 54.2 KJg^{-1}.

FIGURE 4: Graphical determination of reaction rate constant.

It is observed that the reaction rate constant changes with change in amount of PET waste powder and NaOH each. This confirms the second order nature of this saponification reaction as the concentration of PET waste power and NaOH affects the saponification above and below 10 g of PET and 7 g of NaOH.

The saponification of PET waste powder was also studied at temperature ranging from 50°C to 80°C. The reaction rate constant at these range were determined from the respective slope of the plot are presented in Table 3 and Figure 5. It is observed that, in some cases, the plot intercepts at instead of passing through origin, as expected theoretically.

The presence of such a small intersect may be due to difficulties arising in determining the specific conductivity at zero time (C_o) at higher temperature. The Arrhenius plot was also plotted using the values of $\log k_2$ versus $1/T$ (Table 3 and Figure 6). The slope of the curve is −2829 K, from which activation energy obtained was 54.2 KJg^{-1}. The Arrhenius constant was determined using the formula k =
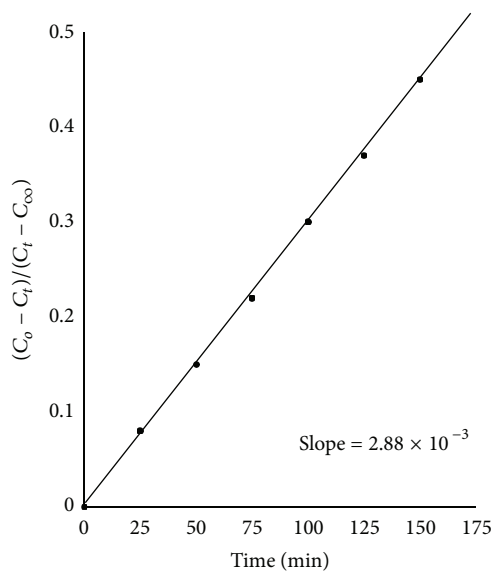
$Ae^{-E_a/RT}$, where k = reaction rate constant at temperature T, E_a = activation energy, R = gas constant, and A = Arrhenius constant. The Arrhenius constant evaluated was 5.0×10^6 Min^{-1}. The other thermodynamic parameters in the saponification reaction of PET and NaOH, such as activation enthalpy, activation entropy, and free energy of activation, were evaluated by Eyring-Polanyi equation [25] using reaction rate constant at various temperatures. A plot of $\log k_2/T$ versus $1/T$ was plotted and, from the slope and intercept of the curve, activation enthalpy obtained was −90.8 KJg^{-1}, while the activation entropy was 126.5 JK^{-1}g^{-1}.
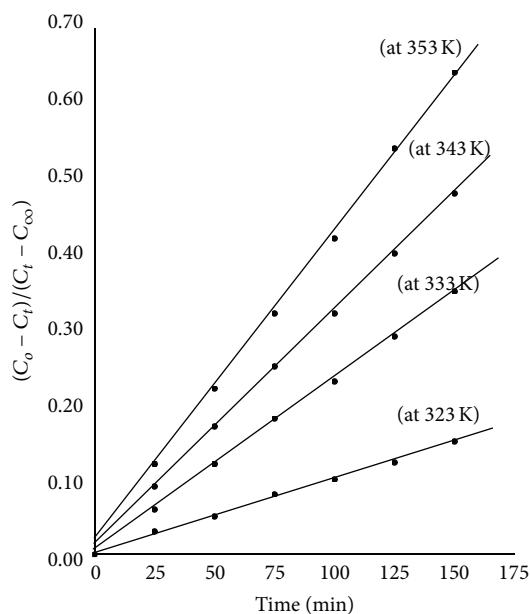
FIGURE 5: Reaction rate constant at different temperature.

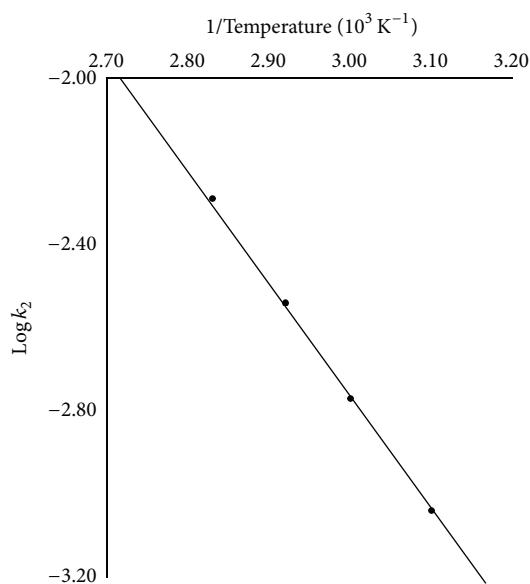FIGURE 6: Arrhenius plot of activation energy.

FIGURE 7: Graphical evaluation of thermodynamic parameters.

TABLE 4: Thermodynamic parameters of saponification.

Temp T/K	$1/T/10^{-3} K^{-1}$	$k_2/10^{-3} g^{-1}s^{-1}$	$\log k_2$	$\log k_2/T$
323	3.10	0.88	−3.05	−9.44
333	3.00	1.68	−2.77	−8.32
343	2.92	2.88	−2.54	−7.41
353	2.83	5.12	−2.29	−6.49

Slope of the graph of $\log k_2/T$ verses $1/T$ = −10925.92.
Intercept of $\log k_2/T$ verses $1/T$ = −4.90.
∴ Activation enthalpy: $\Delta H^{\ddagger}$ = −90.8 KJg^{-1}.
Activation energy: $\Delta S^{\ddagger}$ = 126.5 JK^{-1}g^{-1}.
Free energy of activation: $\Delta G^{\ddagger}$ = 49.9 KJg^{-1}.

They reported high value of activation energy 59.71 KJg^{-1} as compared to the value reported in this work. Such a large variation in the values on activation energy can be attributed to errors associated with gravimetric technique by forming a precipitate of product and its drying and weighing at periodical interval, which is an offline technique.

4. Conclusion

In present work, with online conductivity measurement, it was possible to determine reaction rate constant of saponification reaction of PET waste powder and NaOH. The rapid online measurement of conductivity and use of reflux water condenser minimized the error due to CO_2 pick-up from atmosphere by NaOH solution and evaporation loss of reaction product ethylene glycol during the saponification.

In view of simplicity in experimental arrangement and measurement technique, the conductivity seems to be better technique for this kinetic investigation. Early investigators found the reaction as first order by different technique [1, 2]. Our conductometric study shows the second order

From these two values, free energy of activation obtained was 49.9 KJg^{-1}. (Table 4 and Figure 7).

To ensure the reliability in the kinetic and thermodynamic parameters, we conducted experiments six times at each temperature. Using these data of reaction rate constant at different temperature, the thermodynamic parameters were determined and shown in Table 5. The results show excellent agreement with these thermodynamic parameters with relative standard deviation from 0.8% to 1.5%.

The reaction rate constant and activation energy for saponification reaction, as obtained from the present work, were compared with the data reported by Mishra et al. [2].
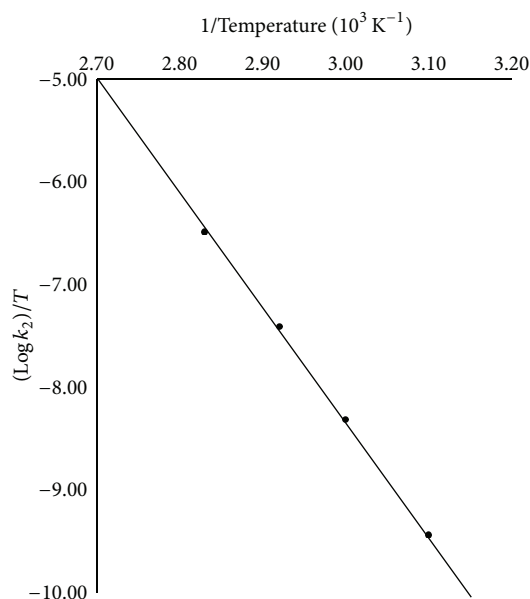
TABLE 5: Statistical data of thermodynamic parameters.

Number of experiments	Activation energy, E_a (KJg^{-1})	Activation enthalpy, $\Delta H^{\ddagger}$ (KJg^{-1})	Activation entropy, $\Delta S^{\ddagger}$ (Jg^{-1}k^{-1})	Activation energy, $\Delta G^{\ddagger}$ (323 K) (KJg^{-1})
1	55.0	91.4	−126.7	50.5
2	53.4	90.2	−123.9	48.5
3	54.3	90.2	−128.8	50.1
4	53.9	90.3	−126.9	49.4
5	54.6	91.4	−126.3	50.5
6	54.0	90.6	−127.5	50.1

Activation energy E_a: 54.2 ± 0.7 kJg^{-1}.
Activation enthalpy $\Delta H^{\ddagger}$: 90.8 ± 0.6 kJg^{-1}.
Activation entropy $\Delta S^{\ddagger}$: -126.5 ± 1.5 Jg^{-1}K^{-1}.
Free energy of activation: 49.9 ± 0.8 KJg^{-1}.
$\Delta G^{\ddagger}$ (323 K).

kinetics since both the reactants were consumed in the reaction. The reaction rate constant had also led to evaluating thermodynamic parameter for this saponification reaction. Our reported value on activation energy is lower and more precise than the value obtained by gravimetric technique reported by Mishra et al. [2].

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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