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Kinetic studies on saponification of ethyl formate by using conductometry method

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ABSTRACT

It is well known from the literature that the saponification of ethyl formate in the presence of a strong base such as sodium hydroxide (NaOH) is a second-order reaction, in which both the reactants are consumed to form sodium formate and ethanol. In the present work conductometric measurement technique has been employed to study the kinetic behavior during the reaction of ethyl formate and sodium hydroxide (NaOH). A laboratory made arrangement with the facility of continuous stirring of solution was used to carry out experiments at desired temperature. The rate constant of saponification reaction at three temperatures (318K, 323K, and 328K) were determined. Chemical kinetics of this reaction indicates that it is a second-order reaction with rate constant $8 \times 10^{-4} \text{ L.mol}^{-1}.\text{s}^{-1}$ at 318 K. From these data, thermodynamic parameters such as activation energy (E_a), activation enthalpy (ΔH^\ddagger) activation entropy (ΔS^\ddagger), and activation free energy (ΔG^\ddagger) have been estimated. With the application of this technique, the determination of rate constant at different solution temperatures becomes simpler and faster.

Keywords: Saponification; Ethyl formate; Rate constant; Thermodynamic parameters; Conductometry

INTRODUCTION

The saponification of esters is one of the most famous reactions in chemistry, and it is represented as a model example of the second-order reaction in the letters dealing with chemical kinetics [1,2]. The saponification of esters has been investigated by a number of investigators at different temperatures using a variety of measurement techniques. Daniels et al. [3] and Smith and Levenson [4] supposed a volumetric titration method independently, in which the composition of reacting mixture was followed by an analysis of sample fractions from the reaction vessel at

specific time intervals. The precision of the method is restricted by the extraction of relevant volume of sample at a fixed duration in addition to errors related with titration using a color indicator. The second technique reported by Stead et al. [5] employs a continuous flow system, where the reactants are consumed continuously at constant temperature in to a stirred vessel. The method utilizes of a large volume of solution. Jensen et al. [6] used high-frequency titrimetry. The method does not require any external indicator or introduction of any electrode

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into the reaction vessel. Another technique written-up by walker [7] depends on conductometric measurements to determine the composition at any given time. The conductometric method avoids periodic removal of samples for analysis and the measurements were carried out manually. This method has already been developed and is used for many miscellaneous applications [8-10] and has been reported by several investigators [11,12].

EXPERIMENTAL

All chemicals used for this work have been purchased from the merck with analytical reagent grade. The stock solution of NaOH (≈ 1 M) and ethyl formate (≈ 1 M) were prepared using distilled water. The standards used in this work were freshly prepared before continuing the experimental campaign. A three-necked round bottom flask is fitted with an internal thermometer, a conductivity measuring cell and a stopper. 100 mL of 0.1 M NaOH solution (0.01 mol) are pipetted in to the flask placed in a water bath. The platinized Electrode surfaces of the conductivity measurement cell and the tip of the thermometer need to be totally submerged in the reaction solution. Using a hotplate stirrer and a contact thermometer the water in the water bath is warmed up to the desired temperature. The ester saponification experiments are carried out at three different temperatures (318K, 323K, and 328K). The hydroxide solution is allowed to equilibrate in the constant temperature water bath. After the thermostating 15 minutes, the sodium hydroxide solution will come to the temperature of the water bath. The temperature should be controlled as precisely as possible. When thermal equilibrium has been reached, the program conductivity is started. In order to calibrate the measuring cell, the cell constant (1.05 cm^{-1}) and the appropriate reaction

temperature are to be entered. The Recording time is set to 100 seconds. Using a micropipette 0.01 mol of the ester (0.82 ml) are added to sodium hydroxide solution while vigorously stirring immediately the sensing software is started by pressing the function key. The series measurements are stored. Fig. 1 shows a schematic diagram of experimental setup.

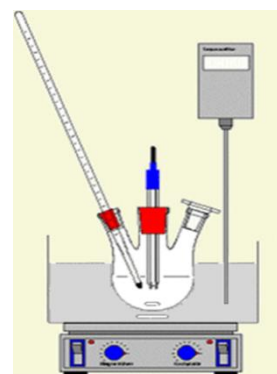
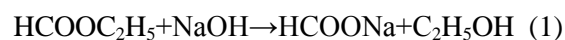


Fig. 1. Experimental setup for the kinetic study.

RESULTS AND DISCUSSION

The reaction of saponification of ethyl formate by NaOH can be shown by the equation 1.



As the reaction progress, hydroxide ions (OH^-) are consumed and formate ions (HCOO^-) are produced. The conductance of an ion depends on its ionic mobility, which in turn is determined by the size of the ion. Since the conductance of the HCOO^- is smaller than OH^- , the conductivity of the reaction solution decreases as the ester saponification progress. Therefore, the progress of the reaction may be monitored by following the change in the electrical conductance of the reaction mixture with time.

From the one set of reaction, the diminution in conductivity was continuously monitored using a conductivity meter. Fig. 2 Shows a graphic

view of conductivity with regard to time during the saponification reaction conducted at a constant temperature. The conductivity of solution during the reaction

at every 100s interval is exhibited on the plot. Conductivity values of solution at each 100s interval were extracted and are shown in Table 1.

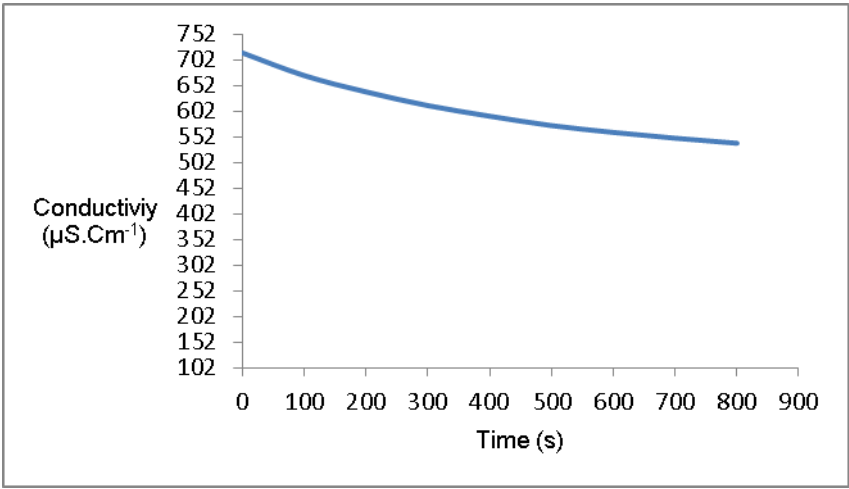


Fig. 2. Real- time plot conductivity versus time for the saponification reaction at a constant temperature solution (318 K).

Table 1. Data for the Computation of Rate Constant in the Saponification Reaction at a Constant Temperature Specific conductance of water ($\kappa_w = 1.4 \mu\text{S.Cm}^{-1}$)
Specific conductance of solution at t ($\kappa_t = \kappa_{\text{soln}} - \kappa_w$)
Specific conductance of solution at t = 0 ($\kappa_0 = 715.3 \mu\text{S.Cm}^{-1}$)
Specific conductance at t = ∞ ($\kappa_\infty = 278.6 \mu\text{S.Cm}^{-1}$)

Time (s)	$\kappa_{\text{soln}} (\mu\text{S/cm})$	$\kappa_t (\mu\text{S/cm})$	$(\kappa_0 - \kappa_t)$	$(\kappa_t - \kappa_\infty)$	$(\kappa_0 - \kappa_t) / (\kappa_t - \kappa_\infty)$
0	715.3	713.9	0	436.7	0
100	671.1	669.7	44.2	392.5	0.11
200	639.4	638	75.9	360.8	0.21
300	612.6	611.2	102.7	334	0.30
400	592.3	590.9	123	313.7	0.39
500	573.8	572.4	141.5	295.2	0.48
600	560.5	559.1	154.8	281.9	0.55
700	549.2	547.8	166.1	270.6	0.61
800	539.4	538	175.9	262.2	0.67
900	529.8	528.4	185.5	252.6	0.73
1000	518.9	517.5	196.4	241.7	0.81

The specific conductivity of reaction mixture before the start of reaction, that is,

at zero time (κ_0), and at various reaction times (κ_t) was measured. The specific

conductivity of water (κ_w) was deducted from various reaction times (κ_t) to get corrected values of κ_0 and κ_t . With the help of corrected values of κ_0 and κ_t , the values of $\kappa_0 - \kappa_t$ were calculated. The values of $\kappa_t - \kappa_\infty$ were obtained by deducting the conductivity at infinity time (κ_∞). From this values of $\kappa_0 - \kappa_t$ and $\kappa_t - \kappa_\infty$ at various reaction times, the values of $(\kappa_0 - \kappa_t) / (\kappa_t - \kappa_\infty)$ were evaluated. A plot of

$(\kappa_0 - \kappa_t) / (\kappa_t - \kappa_\infty)$ against time indicates a straight line passing through origin and shows the second-order kinetics. The rate constant at a constant solution temperature was determined using relation cited in the literature [13,14]. The reaction rate constant at 318, 323 and 328 K were determined from the respective slope of the plot and are presented in Table 2 and Fig. 3.

Table 2. Rate constants of the saponification reaction at different temperatures. (Composition of bath solution: [ethyl formate]₀: 0.1 M; [NaOH]₀: 0.1M)

T (K)	1/T	k (L.mol ⁻¹ .s ⁻¹)	ln k
318	314× 10 ⁻³	8× 10 ⁻⁴	-7.13
323	309× 10 ⁻³	21× 10 ⁻³	-6.16
328	304× 10 ⁻³	28× 10 ⁻³	-5.87

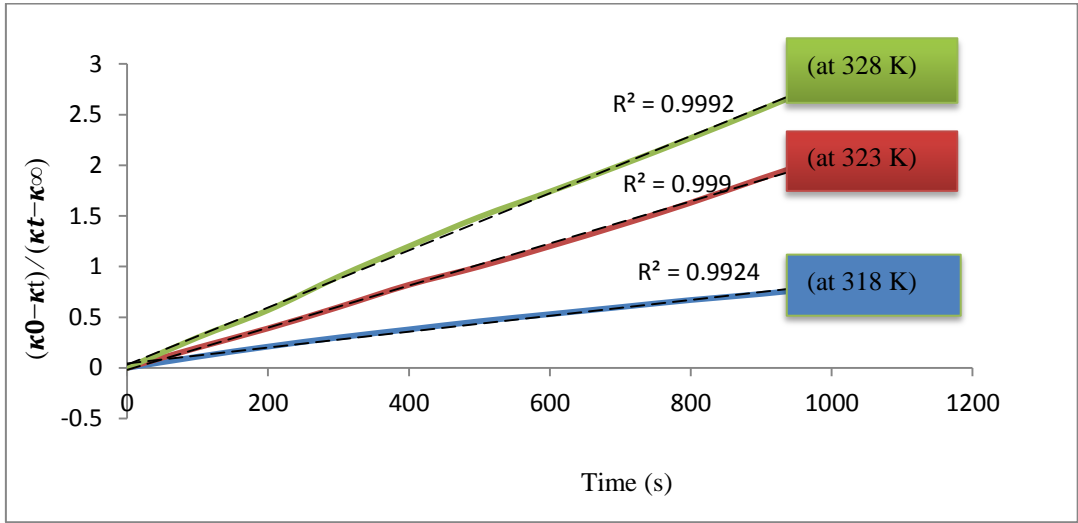


Fig. 3. plots of $(\kappa_0 - \kappa_t) / (\kappa_t - \kappa_\infty)$ against time for the determination of rate constant of the reaction at different solution temperatures. [Ethyl formate]₀: 0.1 M; [NaOH]₀: 0.1 M.

The Arrhenius plot was also plotted using the values of log k versus $1/T$ (Fig. 4). The slop of the curve is -12600, from which activation energy obtained was 104.7 kJ.mol⁻¹ at 318 K. The other thermodynamic parameters in the saponification reaction of ethyl formate

such as activation energy (E_a), activation enthalpy (ΔH^\ddagger), activation entropy (ΔS^\ddagger) and activation free energy (ΔG^\ddagger), were calculated by Eyring-Polani equation [15] and presented in Table 3.

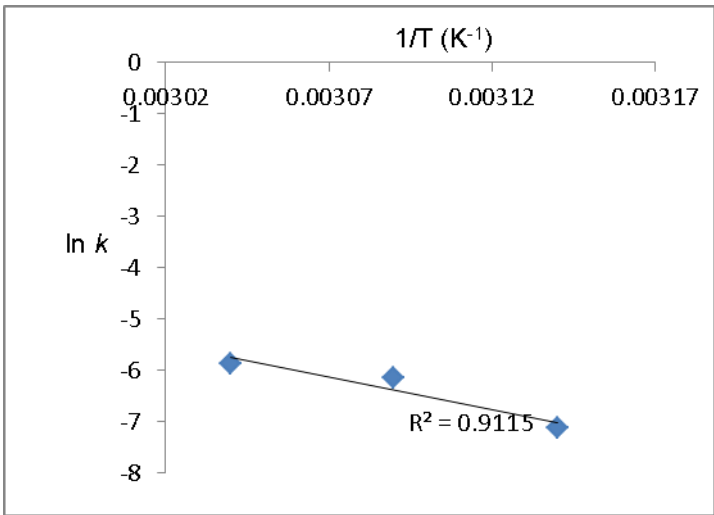


Fig. 4. Arrhenius plot of activation energy.

Table 3. Thermodynamic parameters in saponification reaction.

Number of experiments	E_a (kJ. mol ⁻¹)	ΔH^\ddagger (kJ. mol ⁻¹)	ΔS^\ddagger (J. mol ⁻¹ .K ⁻¹)	ΔG^\ddagger (kJ. mol ⁻¹)
1	104.7	102.1	-16.35	96.9
2	103.9	101.2	-13.52	96.4
3	104.5	101.8	-15.40	95.7
4	103.2	100.5	-16.66	95.2
5	104.8	102.1	-17.61	96.5

CONCLUSION

In present work, with conductivity measurement, it was possible to determine the rate constant of a saponification reaction of ethyl formate by NaOH at different temperatures with high degree of reliability in a much simpler way. This accurate determination of the rate constant to estimate thermodynamic parameters for the saponification. It will be highly useful for researchers to employ this technique for the kinetic study in any other system.

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