

Research Article

Shifting Order Kinetic Study for Alkaline Hydrolysis of Ethyl Acetate

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Abstract

In this research work “The non-integral shifting order” of the alkaline hydrolysis of ethyl acetate reaction was studied. The order shift values of this reaction were studied within the range of [0-1]. The values of k_1 and k_2 were found to be 0.0016 and 3.771 respectively. For shifting order rate equation.

$$\frac{k_1 C_A}{1 + k_2 C_A}$$

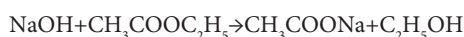
Order shift point corresponds to molar concentration 0.038M. The time-concentration data for kinetic study was based on conductivity measurements.

Keywords: Saponification Reaction; Reaction Kinetics; Rate Constant; Shifting Order Point; Conductivity

Introduction

Chemical reaction takes place when a detectable number of molecules of one or more species have lost their identity and assumed to be in a new form by a change in the kind or number of atoms in the compound and by a change in structure or configuration of these atoms. In this classical approach to chemical change, it may be said that the total mass can neither be created nor be destroyed when a chemical reaction occurs. Saponification reaction is the hydrolysis of a fatty acid in a basic medium. The role of base in the saponification reaction is that it breaks the ester bond and releases the fatty acid salt and glycerol. Esters are usually present in the form of tri-glycerides. Saponifiable substances are those that can be converted into soap after some sort of chemical treatment. Sodium hydroxide is for making hard soaps while potassium hydroxide is commonly used to produce soft soaps. Chemical reaction kinetics is the part of physical chemistry that studies reaction rates. The reaction rate for a reactant or product in a reaction is intuitively defined as how fast or slow a reaction takes place [1-3].

The chemical reaction is as follows:



Conversion can be distinguished into instantaneous or overall conversion. For continuous process both have the same meanings but here as in batch process, there are significant differences. Equilibrium conversion is that condition for reversible reactions at which rate of forward and backward reactions are same. Due to importance of saponification process, several studies had been done on its various aspects, thus hydrolysis of ethyl acetate to produce sodium acetate and ethyl alcohol by treating it with sodium hydroxide is also called saponification reaction although a product is not soap. Previous study shows that highest mole fraction can be achieved when equal flow of both reactants is pumped into the reactor.

The rate equation indicates the effect of changing concentration of reactants on the rate of reaction, to know about all the other things (like temperature, pressure and catalyst) which also change the rate

of reaction, by fitting these parameters into the equation, is so-called rate constant (k). By changing the concentration of reactants, the rate remains constant, but if variation of temperature, pressure or catalyst is observed then rate constant will change accordingly [4, 5].

The general rate equation for shifting order reaction is [6]:

$$-r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A^m}{1 + k_2 C_A^m}$$

where in this case;

$$m = n - 1$$

Order gives the detail about the stoichiometry of the rate determining step of the whole reaction. A reaction can have more than one order depending upon different concentrations of reactants. It is in fact a relationship between concentration of reactants/products and the rate of reaction. It also indicates that to what extent the concentration of reactant affects the rate of reaction, as well as which component has the greatest effect. Similarly, shifting order is a reaction that can have more than one order depending upon different concentration of reactants. For example, a reaction having rate law is found to have a zero order initially when reactants are at high concentrations, while the reaction order shifts to first order at the end of reaction when concentrations of reactants are low. The rate constant decreases as the chemical reaction proceeds. This reduction in rate was the evidence for the initial concentrations of reactant to be approximately same. There are certain rules for which we select the values of m and n reaction [7, 8].

- i. At high concentrations, the order will be $m-n$
- ii. At low concentrations, the order will be m
- iii. Use any values of m and n in the hit and trial method for which order lies within the range that is, $-3 \leq \text{order} \leq +3$

Industrial importance of the reaction product sodium acetate, demands for process improvements in terms of maximum conversion and economical and environmental friendly usage as well. During the reaction, hydroxide ions are consumed and acetate ions are produced.

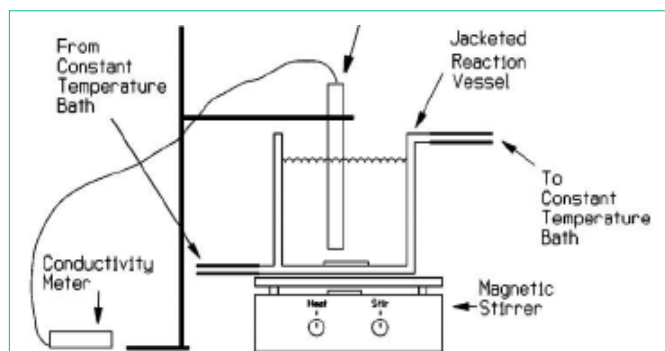


Figure 1: Experimental setup is shown.

Table 1:

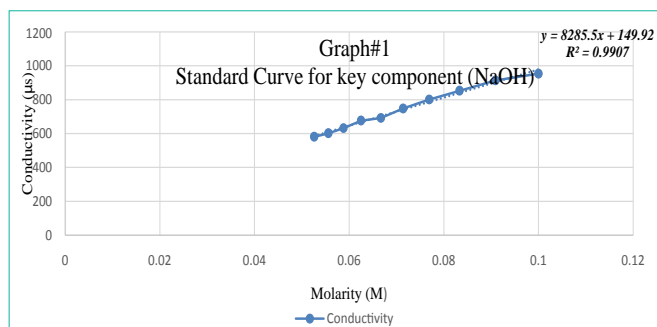
Sno	Time (Mins)	Concentration (μs)	Concentration (M)	$t/C_{A_0}-CA$	$\ln C_{A_0}/C_A$	$-r_A$
1	0	1001	0.1027	-----	-----	1.184×10^{-4}
2	2	443	0.0353	29.673	3.765	4.984×10^{-5}
3	4	398	0.0299	54.940	3.853	4.299×10^{-5}
4	6	373	0.0269	79.155	3.919	3.907×10^{-5}
5	8	356	0.0248	102.695	3.973	3.628×10^{-5}
6	10	346	0.0236	126.422	4.007	3.475×10^{-5}
7	12	338	0.0227	150.000	4.035	3.345×10^{-5}
8	14	333	0.0221	173.697	4.054	3.263×10^{-5}
9	16	328	0.0214	196.801	4.078	3.180×10^{-5}
10	18	325	0.0211	220.588	4.088	3.127×10^{-5}

This change in ionic concentration results in a conductivity change in the solution and by the measurement of this conductivity we could ascertain the degree of saponification. For this purpose, the conductivity of the reaction mixture changes with conversion and therefore the extent of the reaction can be monitored by recording the conductivity with respect to time. This reaction can be followed using conductivity because the molar conductivity of acetate ions is much smaller than the molar conductivity of hydroxide ions. However, there will also be large background conductivity from the Na^+ counter ions from the base [9-11].

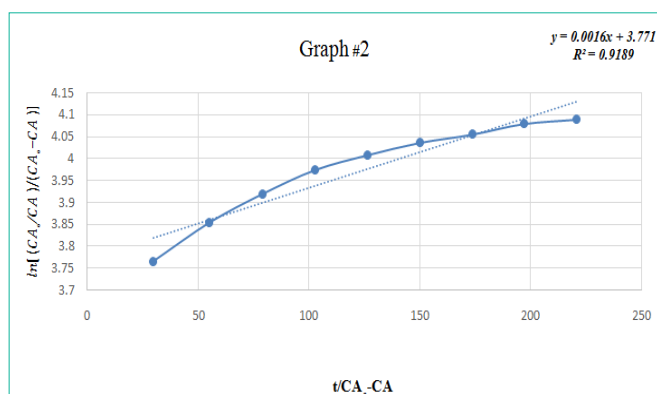
Procedure

This reaction was carried out in a batch reactor with conductometer inserted into the reactor to measure the conductivity of reaction after specific intervals. This conductometer gives the values in (μs) and with the help of standard curve we convert them into molarity (M) units.

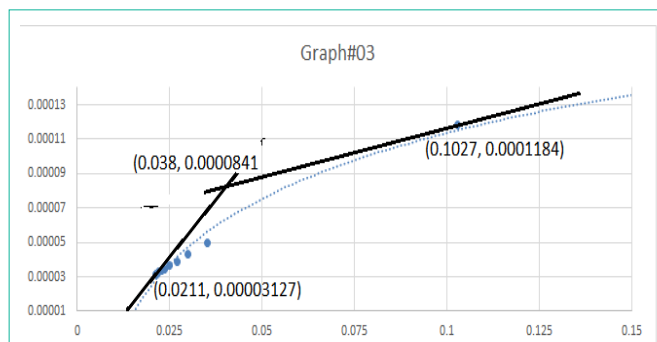
The experimental setup includes; Thermostatted bath, Conductivity meter, Stopwatch, Reaction vessel –Jacketed beaker, volumetric flask, graduated cylinder, pipettes of assorted sizes, burette. The chemicals or reactants required to carry out this reaction are Sodium Hydroxide (NaOH) and Ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$). For batch experiment, equal volumes (100ml) of each reactant are used and initial concentrations of both reactants are 0.1M. The reactants should be close to the same temperature as possible before startup of reaction. Observing the initial conductivities for both the reactants and on conductometer after time intervals of two minutes. This procedure is continued until no change is observed on conductometer



Graph 1:



Graph 2:



Graph 3:

or at least three same consecutive readings were detected. Converting these readings of conductometer into Molarity units with the help standard curve for key component which includes the regression line plotted between Molarity on X-axis and Conductivity on Y-axis (Table 1). Then by plotting a graph 2 between $\frac{t}{C_{A_0}-C_A}$ on X-axis and $\ln \frac{C_{A_0}/C_A}{C_{A_0}-C_A}$ on Y-axis, slope of this graph will give k_1 while intercept will give k_2 . Putting these values of k_1 and k_2 in general rate equation to get

$$-r_A = \frac{k_1 C_A^m}{1 + k_2 C_A} \text{ (where, } m = n = 1 \text{)}.$$

The third graph is between C_A on X-axis and $-r_A$ on Y-axis and then drawing two counter tangents on the curve as shown in graph, the point where these tangents meet will indicate the required concentration on X-axis at which order shifts.

Result

The values observed with the help of conductometer after two

minute intervals are tabulated below. The conversion of (μs) to (M) is done by graph between (μs) at Y-axis and (M) at X-axis, hence regression line will give the equation of straight line, which is $y = 8285.5x + 149.92$ and we obtained values of "x" by putting values of "y". This is called standard curve for key component (NaOH). In this way all the values of Conductivity are converted into Molarity and in next graphs concentrations in terms of Molarity are used. Following table will be constructed after performing experiment as discussed above:

Graphical Presentation

Hence graph #1 shows the straight line equation from which we would be able to determine conductivity in terms of molarity from regression line, the equation of straight line.

$$y = 8285.5x + 149.92$$

With the help of above equation we will convert values of conductometer into Molarity units.

In most of the practical problems and during the laboratory experimentation for studying reaction kinetics, it is observed that the time versus concentration relationships were non-linear which shows "Non-Integral order" nature of the problem. Therefore, the check for shifting order becomes necessary. The graph between $\frac{t}{C_A - C_A^0}$ on x-axis and $\frac{t}{C_A - C_A^0}$ on y-axis is straight line or linear which proves this reaction to be shifting order within the order range of [0 to 1]. Other order ranges may be studied by fitting the data in general rate equation. The values of k_1 and k_2 are obtained from slope and intercept of this graph respectively.

$$y = 0.0016x + 3.771$$

Comparing with straight line equation ($y = mx + c$) we get;

$$m = \text{slope} = k_1 = 0.0016 \text{ Min}^{-1}$$

$$c = \text{intercept} = k_2 = 3.771 \text{ M}^{-1}$$

At high concentration of key component or $k_2 C_A \gg 1$ the reaction is of zero order with rate constant (k) = k_1/k_2 .

Conversely, if concentration is low or $k_2 C_A \ll 1$, the reaction will be of first order and hence transition takes place at $k_2 C_A \cong 1$.

Form graph #3, constructed between and concentration in terms of molarity (C_A) on X-axis and rate ($-r_A$) on Y-axis. It is observed that the concentration at which order shifts is equal to $C_A = 0.038\text{M}$, above this concentration order tends to zero and below this it tends to pseudo first order reaction.

Interpretation of Results

In this research paper hydrolysis of ethyl acetate is studied without agitation using non-integral shifting order analysis.

By graphical method it is proved to be shifting order reaction and then the order shift point was calculated within order range "0 – 1".

Values of k_1 and k_2 are found to be 0.0016 and 3.771 respectively.

Order shift point corresponds to Molar Concentration equal to 0.038M.

The order shift analysis may show the three step reaction mechanism.

Future Prospects and Recommendations

As this saponification reaction is proved to be shifting order within the order range of "0–1" and also order shift point was calculated. This reaction may be further studied for other order ranges like "1–2" or "2–3".

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