

## STUDIES ON KINETIC PARAMETERS OF A SECOND-ORDER REACTION OF HYDROLYSIS

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**Abstract:** The studied reaction is the alkaline hydrolysis of ethyl acetate. The overall order of the reaction is the sum of the orders of the two reagents. The kinetics of the reaction was followed by applying the conductometric method. They worked starting by different initial concentrations of the reactants. Another parameter that has been changed was the temperature. Based on the experimental data, the half-life of the reaction was determined for each individual case. There were established the optimal working conditions for the studied parameters.

**Keywords:** conductometric method, hydrolysis, second-order reaction.

### INTRODUCTION

Reaction of an acid with an alcohol in presence of traces of a mineral or Lewis acid to give an ester as product is called esterification. The reverse reaction, i.e., the splitting of an ester into the component acid and alcohol is known as ester hydrolysis.

In principle, these reactions are reversible, and both reactions can be catalysed either by acids or bases. The acid catalysed hydrolysis reactions are also symmetric, meaning that it is only necessary to reverse the steps to get the mechanism for esterification. But hydrolysis is usually favoured by base catalysis, because the acid formed is removed as the salt, thus driving the reaction forward to completion [1], [2], [3].

The process does not correspond to catalysis in the strict sense of the word, because the hydroxyl ions are consumed in the reaction [4]. The equilibrium is totally shifted to the right due to the stability of the resulting carboxylate ion. A

useful indication of the rate of a reaction is the half-life of a substance, which represents the time when its concentration falls to half the initial value. As a result, a reduced half-life indicates a faster reaction rate. When we start by equal initial concentrations of the two reactants, ethyl acetate and sodium hydroxide, we can calculate the half-life regarding sodium hydroxide by applying the conductometric method [5].

The integrated rate law is:

$$\frac{1}{c_R} = \frac{1}{c_{0R}} + kt \quad (1)$$

where:

$c_R$  - concentration of sodium hydroxide at time  $t$ ;

$c_{0R}$  - concentration of sodium hydroxide at initial time (at  $t=0$ );

$k$  = rate constant of the reaction.

The calculated half-life  $t_{1/2}$  is:

$$t_{1/2} = \frac{1}{k \cdot c_{0R}} \quad (2)$$

The conductance dependence on the concentration of sodium

hydroxide in the reactant mixture is given by the relations:

$$c_R = \text{constant} (G_t - G_f) \quad (3)$$

$$c_{0R} = \text{constant} (G_0 - G_f) \quad (4)$$

where:

$G_0$  - the conductance of the reactant mixture at the initial moment;

$G_t$  - the conductance of the mixture at time  $t$ ;

$G_f$  - the conductance of the mixture corresponding to the total hydrolysis of the ester.

### EXPERIMENTAL PART

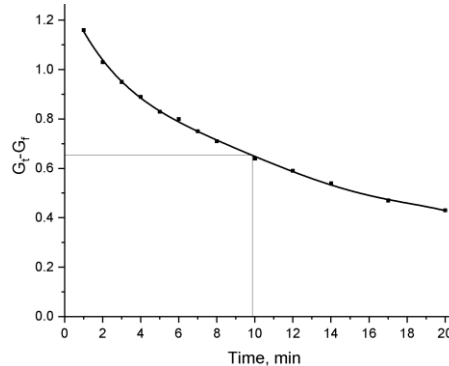
Solutions of sodium hydroxide and ethyl acetate of equal concentrations were prepared. Equal volumes of solutions of the same concentration of sodium hydroxide and ethyl acetate were mixed. The moment of mixing corresponds to the initial moment, against which the determinations were made. For each initial mixture, the conductance was measured for 20 minutes. Measurements were done for the reaction mixture maintained at 20°C, 24°C, and 28°C, respectively. To complete the reaction, a sample identical to the one measured at any of the three temperatures was kept in the water bath at 60°C for 30 minutes. Later then it was cooled and it was measured the conductance. The same procedure was followed for all samples.

It was aimed to determine the optimal conditions in the ranges of values studied, so that the half-life is minimal. The optimal conditions were obtained using the method of factorial experiments [6].

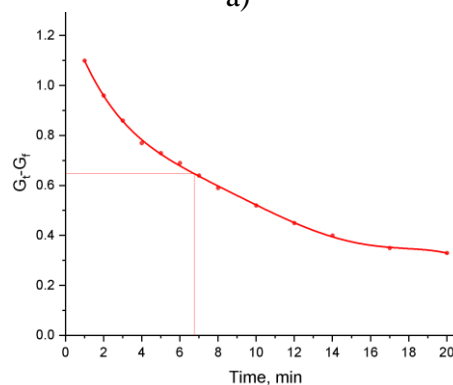
ANOVA test was used to analyze the variations between the experimental data.

### RESULTS AND DISCUSSIONS

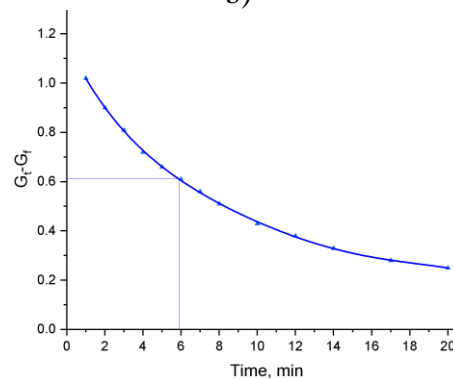
The results of the conductance measurements for the reactant mixtures of different concentrations at different temperatures, for 20 minutes, were processed in order to obtain the half-life time.



a)



b)



c)

Figure 1. The variation with time of the concentration of sodium hydroxide starting by 0.02M, at working temperatures of 20°C (a), 24°C (b) and 28°C (c).

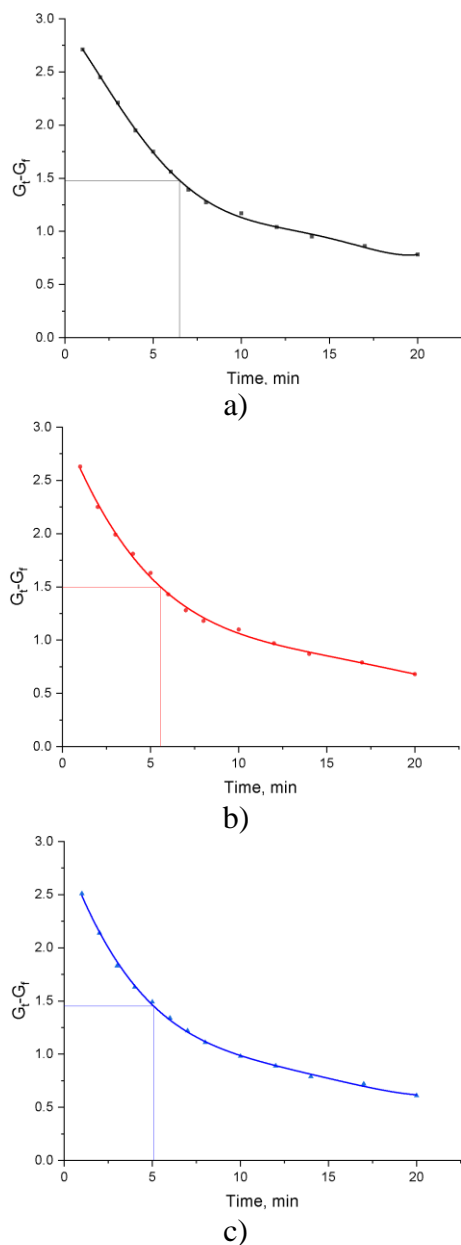


Figure 2. The variation with time of the concentration of sodium hydroxide starting by 0.04M, at working temperatures of  $20^\circ\text{C}$  (a),  $24^\circ\text{C}$  (b) and  $28^\circ\text{C}$  (c).

The variation with time of the concentration of the reactant in this second-order reaction is presented in figures 1-3. You may notice the obtained half-lives in these graphic illustrations, shown in figures 1 for solutions of initial concentrations of

0.02 M, in figures 2 for solutions of initial concentrations 0.04 M, respectively in figures 3 for initial concentrations 0.06M.

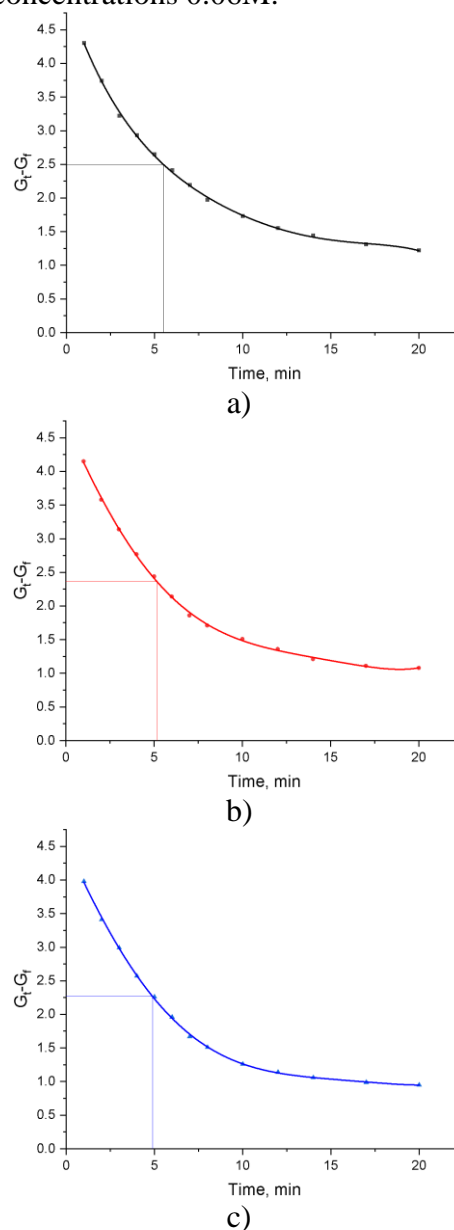


Figure 3. The variation with time of the concentration of sodium hydroxide starting by 0.06M, at working temperatures of  $20^\circ\text{C}$  (a),  $24^\circ\text{C}$  (b) and  $28^\circ\text{C}$  (c).

The temperature and concentration factors at three levels were considered, and the half-life time as a response function. A full factorial

experiment containing 27 experiments was carried out.

The experimental matrix is presented in Table 1.

Table 1. Experimental matrix

		Factor 1	Factor 2	Response 1
Std	Run	A:Conc	B:Temp	Time
7	1	0.02	28	6.43268
6	2	0.06	24	5.1441
12	3	0.06	20	5.48818
17	4	0.04	28	5.08501
10	5	0.02	20	9.85127
2	6	0.04	20	6.49101
18	7	0.06	28	4.8884
4	8	0.02	24	6.7509
21	9	0.06	20	5.65056
11	10	0.04	20	6.69143
13	11	0.02	24	6.98357
25	12	0.02	28	6.56118
22	13	0.02	24	6.52057
14	14	0.04	24	6.49101
24	15	0.06	24	5.30273
23	16	0.04	24	5.82213
1	17	0.02	20	10.1537
5	18	0.04	24	5.29157
27	19	0.06	28	4.97981
3	20	0.06	20	5.3212
9	21	0.06	28	4.79852
19	22	0.02	20	9.55144
20	23	0.04	20	6.35395
8	24	0.04	28	5.19103
15	25	0.06	24	5.05
16	26	0.02	28	6.30628
26	27	0.04	28	4.94525

The ANOVA test allowed the assessment of whether the differences between the experimental data are due to random errors or systematic effects of the experiments. It also allows

examining the significance of factors in a multifactorial experiment.

Table 2. ANOVA test results

Source	Model	A-Conc	B-Temp	AB
Sum of Squares	55.39	30.34	16.07	8.98
Mean Square	6.92	15.17	8.04	2.25
F-value	100.93	221.12	117.13	32.73
p-value	< 0.0001	< 0.0001	< 0.0001	< 0.0001
	significant			

The statistical test for ANOVA is the Fischer test (F test). Table 2 shows that the value of the F test is 100.93, which means that the model is significant.

The *p*-value is widely used in statistical hypothesis testing. P values less than 0.0500 indicate that the model terms are significant. In this case, A, B, AB are significant model terms.

The regression model is given by the following relationship:

$$y = 6.23 + 1.45 \cdot A1 - 0.4078 \cdot A2 + 1.06 \cdot B1 - 0.2973 \cdot B2 + 1.12 \cdot A1 \cdot B1 + 0.3637 \cdot A2 \cdot B1 - 0.6301 \cdot A1 \cdot B2 + 0.3475 \cdot A2 \cdot B2 \quad (5)$$

The coded terms equation (5) can be used to make predictions about the response for given levels of each factor. The coded equation (5) can determine the relative influence of factors by comparing factor coefficients.

The significance of the factors in relationship (5) is shown in Table 3.

Table 3. Factor semnification

Concentration, %			Temperature, °C		
Value	A1	A2	Value	B1	B2
0.02	1	0	20	1	0
0.04	0	1	24	0	1
0.06	-1	-1	28	-1	-1

The response surface obtained from the graphical representation of the experimental data is presented in figure 4.

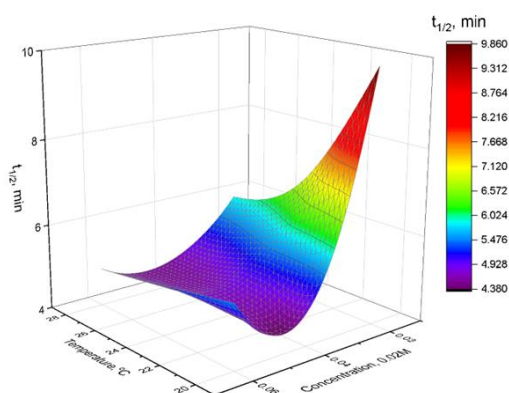


Figure 4. Response surface: half-life depending on concentration and temperature.

From figure 4 you can see the dependence of the half-life according to the process parameters. It is noted that the half-life decreases with increasing concentration and increasing working temperature.

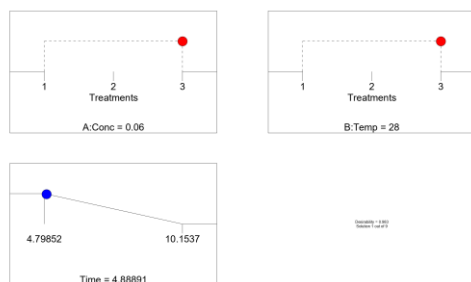


Figure 5. The optimal combination of process parameters that provides the lowest half-life.

Based on the regression model expressed by relationship (1), the optimal combination that provides the lowest half-life in the ranges of values established for concentration and temperature can be determined (figure 5).

Using the "Parallel plot" representation (figure 6) one can identify the optimal combination of parameters for which the minimum half-life is obtained. The highlighted curve represents the optimal combination of parameters which provides the lowest half-life.

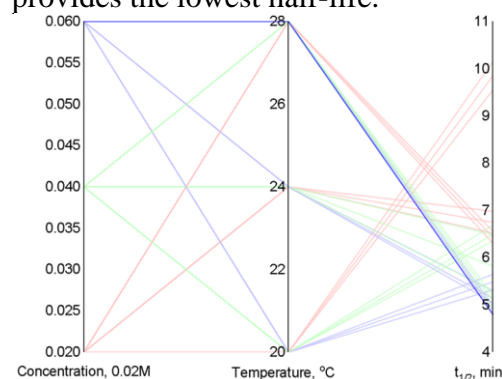


Figure 6. Parallel plot.

## CONCLUSIONS

In the alkaline hydrolysis reaction, there is an exchange between ions of different mobilities, namely the more mobile hydroxyl ions are replaced by the less mobile acetate ions, changing the conductance of the reactant mixture.

Gathering the results of the half-lives determined graphically, it can be observed that the values decrease with the increase of the hydrolysis temperature for the reaction mixtures of the three different initial concentrations. This indicates an increase in the rate reaction in the same direction.

If the hydrolysis is maintained at a certain temperature, it was found

experimentally that the rate reaction increases by increasing the initial concentrations of reactants.

The paper presents an experimental method for determining the half-life of the alkaline hydrolysis reaction of ethyl acetate.

The use of factorial experiments presents several advantages such as:

- using the method of factorial experiments, there were possible simultaneous testing of the two factors and the interaction between them;

- the main effects and the interaction between the considered factors were identified and the regression model that mathematically describes the esterification process in the considered interval was determined;

- using the method of factorial experiments, the most favorable combination was identified in order to obtain a very low half-life.

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