MODERN STUDY OF BEHAVIOR SUCROSE

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Abstract: The disaccharides called sucrose not hydrolyze in aqueous solution; the reaction is known as sucrose inversion, is catalyzed by mineral acids, and can be studied by the polarimetric method. Treaties chemical kinetics fit this kind of reaction order n = 1, [1- 4]; the reaction rate depends on the concentration of sucrose, being considered a chemical reaction of zero order towards water. Specialty papers mention that the order of reaction might be determined by graphical integral method; plot, towards values of reaction times, four functions of sucrose concentration (c_t, $\ln c_t$, $1/c_t$, $1/2c_t^2$). This paper proposes a modern kinetic study on acid hydrolysis of sucrose, without mechanical agitation of reactant mixture. The multiple measurements were made with automatic polarimeter, and objective experimental results were processed with a computer; the software offers additional information on the dispersion of experimental data, and the results are outstanding.
Keywords: sucrose, hydrolyze, acid medium, optical activity, kinetic parameter

1. Introduction

We start from the belief that the study results mentioned reaction kinetics are dependent on: the behavior of reactant, limits quantitative method of investigation and mathematical processing device limits of the experimental results. The literature includes transformation by acid hydrolysis of sucrose - known as sucrose inversion - in the category of chemical reactions of order n =1. Sucrose and its hydrolysis products – glucose and fructose - are optically active substances. Considering that, the hydrolysis reaction is irreversible

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6\,(gl) + C_6H_{12}O_6\,(fr) \quad (1)$$

The authors considered that the transformation reaction mixture can be studied by optical business value; value of the optical activity of the mixture should fall to negative values due to fructose. At any time t, molar concentration of sucrose, c_t is calculated with

$$c_t = \alpha_t - \alpha_f \quad (2)$$

where [5]:

- α_t - value of optical activity reactant mixture, in any moment, when hydrolyzed part of the amount of sucrose,
- α_f - optical activity value at the end of hydrolysis process; we found that this value is not reproducible.

To conduct a study polarimeter reactant mixture - between measurements is introduced in a thermostatic chamber and using a classically polarimeter - is found that:

1. The experimental values have a normal evolution, but some are surprising (much higher or much lower).

2. By plotting the concentration functions - only for integer values of the order of reaction - value pairs defined in the plan only curves.

In this case, we considered that the experimental assembly is designed poorly, and is not the best processing experimental values. The two previous findings have led to the improvement of experimental assembly and method of processing and interpretation of experimental values, as follows:

- study of the reactant mixture molar concentration of sucrose is very small, so that the mixture density is very close to that of the solvent (distilled water);
- avoid mechanical stirring reaction mixture (the polarimeter tube is maintained and thermostated in working position);
- using an automatic polarimeter;
- the automatic polarimeter is associated with a Windows operating system to take over and processing of experimental results [6];
- a method of calculating the molar concentration of sucrose, taking into account the contributions of all asymmetric chemical species that are present in the reactant mixture;
- determination of kinetic parameters of reaction by differential graphically method.

By using the proposed experimental assembly and processing of the experimental values are obtained interesting conclusions.

2. Materials and experimental methods

For the kinetic study, prepare reagents, glassware and laboratory equipment, as follows.

Reagents: double distilled water and two solutions, ($1g_{sucr}$ /100 mL) one stock solution of sucrose and 1N HCl, reagents Merck booth.

The glassware and laboratory equipment: pipettes (5, 10, 25 mL), flasks (25, 100 and 500 mL), glasses, analytical balance, computer with operating system Windows, automatic polarimeter (Atago, type AP-300, $\lambda = 589\,\mathrm{nm}$, the polarimeter tube has length $l = 200\,\mathrm{mm}$, with RCS-232 interface to Windows; the proper intern software is HyperTerminal), thermostat liquid unity with recirculation (20-80ºC, type Pye Unicam) and tool temperature control (Digital thermometer, tip Optronic, Krüss).

2.1 Experimental conditions

Polarimeter tube was placed inside a cylindrically thermostatic unity (connected in fluid circuit) and working temperatures were strictly controlled, 20ºC. Polarimeter tube filled with reactant mixture is always in working position.

2.2 Experimental measurements

The reactant mixture comprises: 5 mL stock solution of sucrose, 10 mL solution of hydrochloric acid and 10 mL double distilled water; the initial concentration of sucrose is $c_0 = 0.2\,\mathrm{g}/100\,\mathrm{mL}$. Was obtained 1750 experimental values of $(\alpha_t)^\circ$. The automatically measured values are obtained successively at intervals of one minute. The software retrieves and stores the α_t values. By Excel, these values are converted into molar concentrations of sucrose c_t and then processed.

2.3 The transformation of α_t values in c_t values

To calculate the specific rotation of asymmetric substances, expressed in sexagesimale degree, „^{0}” the polarimeter AP-300 us the formula:

$$[\alpha^{\circ}]_D^{20} = \frac{10000 \times \alpha}{1 \times c\,(g/100\,mL)} \quad (3)$$

where: (α°) is the optical activity of a solution of concentration c (g/100 mL) measured in a polarimeter tube size l (mm).

The specific rotation values of the three saccharides – sucrose, glucose and fructose – are: $[\alpha_{sucr}] = +66.5^{\circ}$, $[\alpha_{gl}] = +52.5^{\circ}$ and $[\alpha_{fr}] = -133^{\circ}$. In the initial moment, $t = 0$, the experimental values describing the sucrose's contribution is in relation,

$$66.5^{\circ} = \frac{10000 \times \alpha_0}{200\,mm \times (0.2\,g_{sucr}/100\,mL)} \quad (4)$$

so as to $\alpha_0 = 0.266^{\circ}$.

The sucrose hydrolysis, equation (1), involves transformation into equimolar mixture of glucose and fructose. We suppose that after t minutes, x_t g sucrose were hydrolyzed, so that the reaction mixture contains:

$$m_{sucr} = (0.2 - x_t)\,g\,; \quad m_{gl} = m_{fr} = 0.5263 \times x_t\,g \quad (5)$$

The total optical activity of reactant mixture α_t, is the sum of optical activities of all sugars present

$$\alpha_t = \alpha_{sucr(t)} + \alpha_{gl(t)} + \alpha_{fr(t)} \quad (6)$$

The sucrose contribution may be calculated, knowing that:

$$[66.5^0] = \frac{10000 \times \alpha_{sucr(t)}}{200 \times (0.2 - x_t)} \quad (7)$$

thus

$$\alpha_{sucr(t)} = (0.266 - 1.33 \times x_t) \quad (8)$$

The glucose contribution is

$$[52.5^0] = \frac{10000 \times \alpha_{gl(t)}}{200 \times 0.5263 \times x_t} \quad (9)$$

$$\alpha_{gl(t)} = 0.5526 \times x_t \quad (10)$$

The fructose contribution is

$$[-133^0] = \frac{10000 \times \alpha_{fr(t)}}{200 \times 0.5263 \times x_t} \quad (11)$$

$$\alpha_{fr(t)} = -1.399958 \times x_t \quad (12)$$

The algebraic sum of the three contributions is:

$$\alpha_t = 0.266 - 1.33 \times x_t + 0.5526 \times x_t - 1.399958 \times x_t \quad (13)$$

$$\alpha_t = 0.266 - 2.177358 \times x_t \quad (14)$$

and may calculate the amount of sucrose consumed

$$x_t = \frac{0.266 - \alpha_t}{2.177358} \text{ g}_{\text{sucr}} / 100 \text{ mL} \quad (15)$$

Using x_t value is calculated the amount of unhydrolyzed sucrose per 100 mL solution and its molar concentration

$$c_t = \frac{(0.2 - x_t) \times 10}{342} = (0.2 - x_t) \times 0.02923 \text{ mol/L} \quad (16)$$

The c_t values obtained are used in kinetic study.

2.4 The verification of experimental assembly

The polarimeter tube was charged with a solution of sucrose, c = 0.2 g sucr/100 mL, and for 165 minutes, were measured optical activity; the calculated value is $\alpha_0 = 0.266^\circ$. The values $(\alpha_t)^\circ$ was plotted and calculated values of the statistical parameters of normal distributions, fig 1 and table 1.

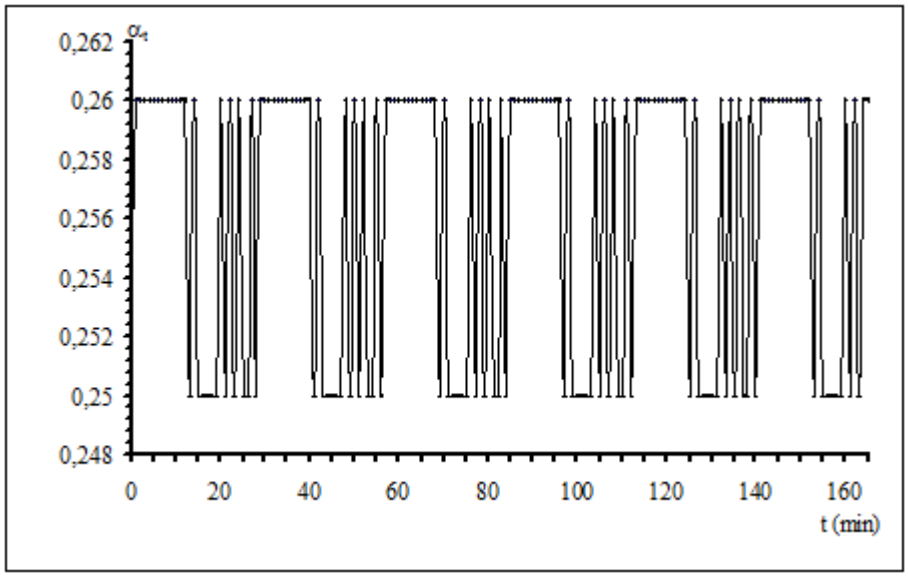

Fig. 1. The graphical representation of the pairs of values $\alpha_t = f(t)$, t=0-165 min

According to figure 1, the population consists only of two experimental values are taken incidentally. According to table 1, are observed very close values of the statistical parameters of trend and very small values of statistical parameters of scattering. The graphical representation and the content of table confirm the stability of sucrose in solution and stability proposed experimental assembly.

Table 1. The values of the statistical parameters of normal distributions for population α_t

The values of the statistical parameters			
Statistical parameters of trend		Statistical parameters of scattering	
arithmetic mean	0.256145	standard deviation	0.003963
median	0.26	dispersion	0.000015
module	0.26	amplitude	0.01
central value	0.255	-	

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3. Interpretation of results

To study the behavior of sucrose acid hydrolysis reaction must be interpreted the 1750 pairs of values ($c_t = f(t)$); figure 2 shows the diagram that describes the evolution of the value of the molar concentration of sucrose to entire domain of time.

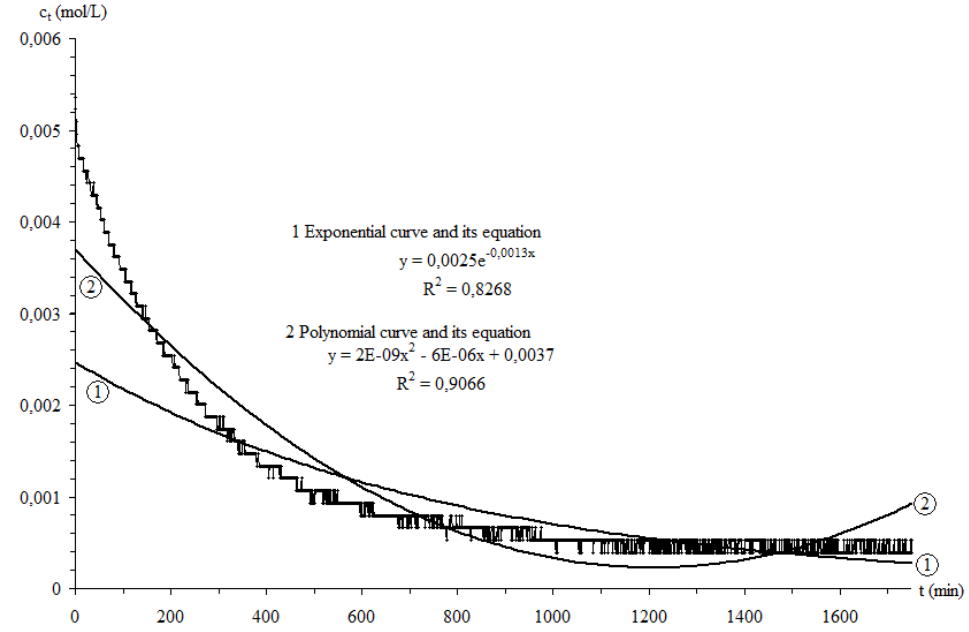

Fig. 2. Graphical representation of the 1750 values of molar concentration of sucrose with curves that describe the exponential and polynomial trend disposition thereof

Noting layout plan of the 1750 pairs of experimental values with exponential and polynomial trend, we can formulate the following four general conclusions.

1. Molar sucrose concentration value decreases. The reduction in molar concentration of sucrose is done in steps, not continuous. Figure 2 shows the successive intervals of time where the molar concentration of sucrose remains constant (successive levels of concentration); in timing units, the amplitude of these intervals increases over

time. It may be considered that in some point of time, hydrolyze a group of molecules sucrose. The penultimate concentration level is recorded at $t = 975\ min$, characterized by the following experimental values: $\alpha_{975} = -0.13^{\circ}$ and $c_{975} = 5.3 \times 10^{-4}\ mol/L$. The last recorded concentration level is at $t = 1142\ min$, characterized by the following experimental values: $\alpha_{1142} = -0.14^{\circ}$ and $c_{1142} = 3.9 \times 10^{-4}\ mol/L$. After this moment the reactant mixture begin a process of chemical equilibrium, when the molar concentration of sucrose oscillating between two values, $\alpha_t = -0.13^{\circ}$ and $\alpha_{975} = -0.14^{\circ}$. The $t = 975\ min$ value became a reference value. According the reference value, the experimental population values are distributed in two domains, as follow: the kinetic domain, containing experimental results values with $t < 975\ min$ and the domain of reversible equilibrium, characterized by values $t = 976\text{-}1750\ min$. Reduction steps molar concentration of sucrose suggests that acid hydrolysis reaction adopt a specific mechanism; the associated sucrose molecules adopt a specific orientation.

To support the design on the association of sucrose molecules, we compare the diagrams $c_t = f(t)$ obtained in three different stages. Thus, fig 3 present the diagram obtained in the first stage considered. The diagram describes the behavior of molecules of sucrose in concentrated solution.

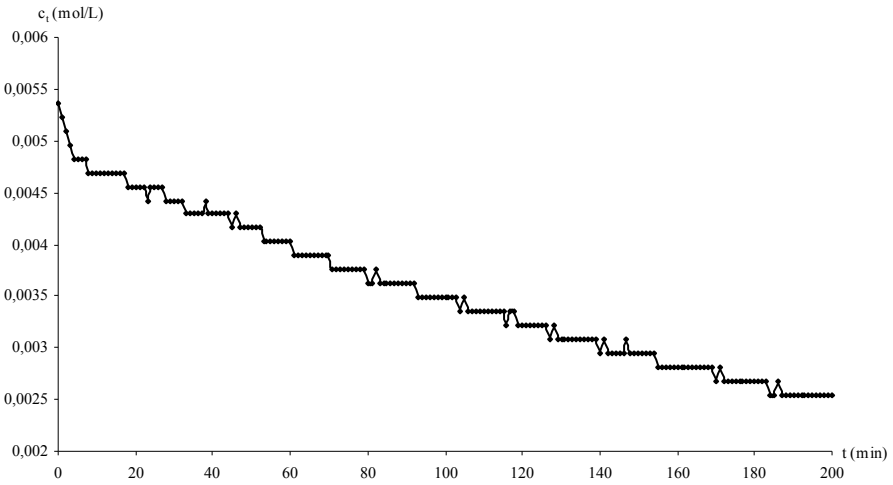

Fig. 3. The diagram higher molar concentration of sucrose in the range t = 0-200 min

Switching from a higher level of concentration to a lower level is made only after sucrose and water molecules were associated appropriate; molecules in favorable association hydrolyze, reducing the concentration of sucrose molar. The unfavorable molecular associations are destroyed, so that - in some cases - reactant mixture returns to the previous concentration level. Any crossing molar concentration value between two adjacent levels can be considered as an unstable chemical equilibrium.

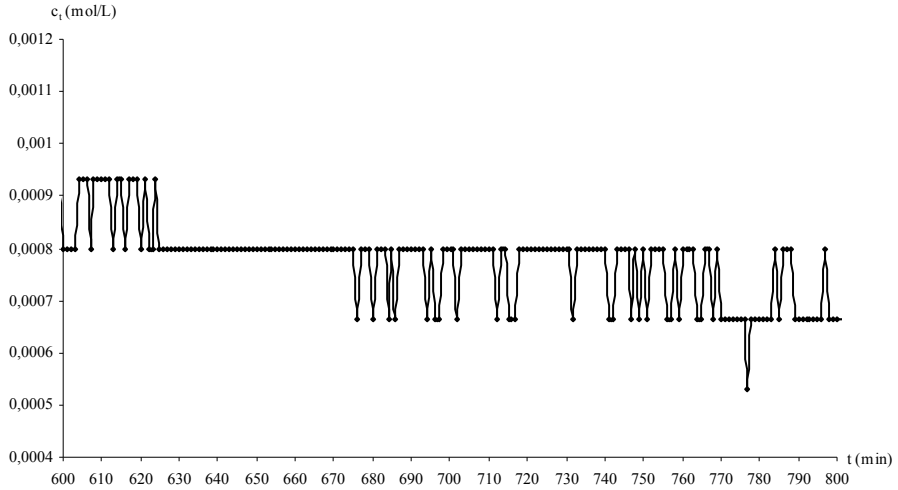

Fig. 4. The diagram medium molar concentration of sucrose in the range t = 600-800 min

The figure 4 contains a diagram that describes the behavior of molecules in the reaction mixture with medium level of sucrose concentration. In the diagram are present only three levels of concentration, but chemically unstable equilibrium frequency becomes high; per unit of volume, decreases the number of favorable molecular association's for hydrolysis process.

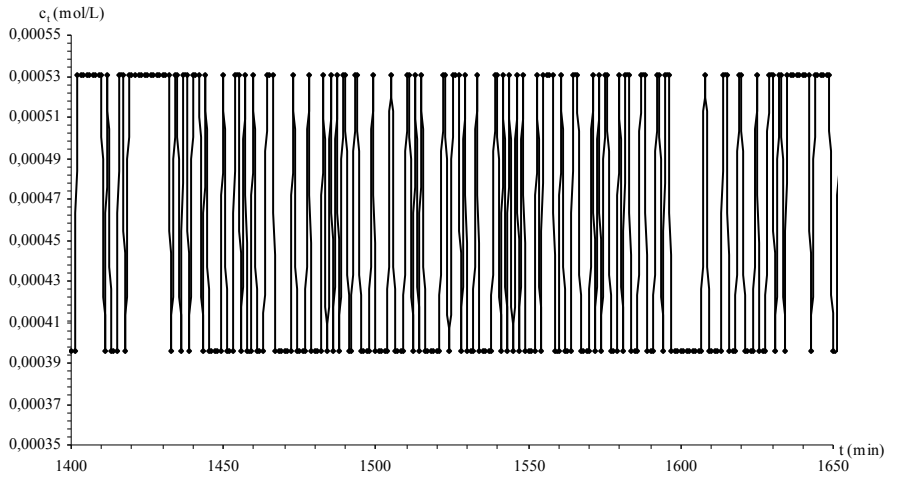

Fig. 5. The diagram lower molar concentration of sucrose in the range t = 1400-1650 min

Observing the diagram of figure 5, we say that lower molar concentration of sucrose is associated with high frequency of unstable chemical equilibrium; due to their high frequency, reactant mixture entered the classical chemical steady state.

2. The trend of experimental pair's values to be distribute on a downward exponential curve is expressed by the equation

$$c_t = 0{,}0025 \times e^{-0{,}0013 \times t} \quad (17)$$

$R^2 = 0{,}8262$, the value for the regression factor is small; this equation can not be used to carry out a complete kinetic study.

3. The trend of experimental pair's values to be distribute on a downward polynomial curve is expressed by the equation

$$c_t = 2 \times 10^{-09} \times t^2 - 6 \times 10^{-06} \times t + 0{,}0037 \quad (18)$$

which has a high value of regression factor, $R^2 = 0{,}9066$; it can be used to characterize the time evolution of reactant mixture. According the polynomial curve, in the reactant mixture, the molar concentration of sucrose decreases exponentially and then begin to take a slight upward trend.

4. Operating model allows to calculate the degree of hydrolysis at any time; it is noted that the degree of hydrolysis falls in

$$\alpha_{h_t} = 10.56 - 93.23\% \quad (19)$$

The sucrose hydrolysis is partial; reactant mixture adopts steady state value when

$$\alpha_{h_t} = 90.93\% \quad (20)$$

4. Conclusions

The content of this paper highlights the following contributions:

1. The superiority of analytical assembly which functions automatically and rigorously controlled experimental conditions, without mechanically stirring.

2. The superiority of processing and interpretation mode of experimental values, providing objective and continuous characterization of reactant mixture. This paper highlights the stage where the reaction is direct and the stage when it becomes reversible.

3. We obtain information which opens the prospect of a kinetic study on the mechanism (highlighting molecular associations), on kinetic and energy parameters.

4. This paper highlights the maximum degree of acid hydrolysis of sucrose.

5. References

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