SUPPLEMENTARY MATERIAL

Practical aspects of the analysis of the progression curves of first and pseudo-first order reactions

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The algorithm of iterative selection of limit value of $Y_\infty$ of the measured parameter was shown in the diagram below (Figure 1S).

where:
- $R^2$ – coefficient of determination
- $\varepsilon$ – predefined accuracy
- $Y_\infty[i]$ – successive value out of the ten elements of a scanned interval
- $t$ – time

**Figure 1S.** The algorithm of iterative selection of optimum limit value of $Y_\infty$, opt of the measured $Y$ parameter of a reacting system
EXPERIMENT

The chemicals used were of analytical grade (HCl, NaOH, sucrose, ethyl acetate, phenolphthalein POCh, Gliwice). All solutions were prepared in redistilled water. Measurement of the change the conductivity was carried out using the multimeter (CX-551, ELMETRON, Poland), magnetic stirrer motor ((Alchem Group OMC ENVAG Sp.z.o.o) and conductivity sensor (EPS-2ZE, k=0,5±0,1). Measurement the angle of rotation the polarized light was carried out using polarimeter Carl Zeiss Jena 228.554. U1 VEB MLW Prüfgeräte-Werk (Germany) thermostat was used for temperature control.

The kinetics of acidic hydrolysis of an ester

47.5 ml of hydrochloric acid with a concentration of 0.8 mol/L was poured into a conical flask (reaction vessel) and placed in a water bath at 25 °C. Once the temperature had stabilised, 2.5 ml of ethyl acetate was added and the concentrations of the acetate acid being produced were started to be determined by means of alkalimetric titration using NaOH solution with a concentration of 0.2 mol/L. Titration was carried out at 10-minute intervals. In order to determine $V_\infty$ experimentally, one sample was titrated three times at one-day intervals, whereas the second one was heated and subsequently, after cooling to a temperature of 25°C, $V_\infty$ was determined.

The kinetics of sucrose hydrolysis

20 ml of hydrochloric acid with a concentration of 0.8 mol/L and 20 ml of sucrose solution with a concentration of 20% or 10% were mixed. The values of the rotation angle of a plane of polarised light ($\alpha$) were being read at 10-minute intervals. In order to determine $\alpha_\infty$ experimentally, for one sample, the value of $\alpha_\infty$ was measured after a day, whereas the other sample had been heated and subsequently, after cooling to a temperature of 25°C, the value of $\alpha_\infty$ was determined.

The kinetics of base hydrolysis of an ester

A mixture of NaOH solution in water and ethyl acetate was prepared with the following final concentrations: 0.01 mol/L of NaOH and 0.01 mol/L of ethyl acetate. While the sample was being mixed, the measurement of conductivity begun. The measurements were repeated respectively for two, four and eight times higher concentrations of ester solution at the same concentration of NaOH. Progression curves were recorded conductometrically. Due to a relatively high reaction rate and thus the ability to determine the asymptote (k∞) without the change of conditions (e.g. heating), recording had been performed at a temperature of 25°C until the value of conductivity stabilised.

RESULTS AND DISCUSSION

Analysis of the kinetics of acidic hydrolysis of an ester

As part of their laboratory class on chemical kinetics, students carried out a reaction involving acidic hydrolysis of an ester (ethyl acetate). The results of this experiment were shown in Table 1S.
**Table 1S.** The data on the progress of ethyl acetate hydrolysis reaction in approx. 0.8 mol/L HCl

| time t [min] | V, mL |
|--------------|-------|
| 0            | 6.9   |
| 10           | 7.1   |
| 20           | 7.3   |
| 30           | 7.5   |
| 40           | 7.7   |
| 50           | 7.85  |
| 60           | 8.0   |
| 70           | 8.15  |
| 80           | 8.3   |
| 90           | 8.4   |
| 100          | 8.5   |

**Figure 2S.** The experimental (points) progression curve and the progression curves calculated on the basis of parameters determined using the nonlinear fitting method (dashed line) and after the reaction was completed by heating the mixture (solid line).

The line obtained by iterative fitting was not shown in Figure 2S and 3S, since its progression was consistent with the line produced by the nonlinear fitting method. Looking at Figure 2S makes it clear that the fitting using an experimentally determined value of $V_\infty$ is much worse (even despite the better quality of measurements). Higher value of $V_\infty$ means reduced range of conversion (extent of reaction) for the analysed data, which, as was shown in point 3, has a significant impact on the quality of fitting.

The complete characteristics of measurement data from Table 1S were shown in Table 2S.
Table 2S. The calculated and the experimentally determined values of $V_\infty$ and their corresponding values of rate constants together with the statistical assessment

| Parameter | The method of determination of $V_\infty$ | 
|-----------|-----------------------------------------|
|           | nonlinear | iteratively | after heating | after three days |
| $V_\infty$ | 9.967724 | 9.849 | 11.45 | 11.65 |
| k         | 0.00752 | 0.00797 | 0.004415 | 0.004184 |
| SD_k      | 6.22E-5 | 6.41E-5 | 7.75E-05 | 7.73E-05 |
| R^2       | 0.99938 | 0.99942 | 0.997232 | 0.996939 |
| $\beta$   | 0.52 | 0.54 | 0.35 | 0.34 |

where: k – observed reaction rate constant [1/min]
SD_k – standard deviation of the rate constant
R^2 – coefficient of determination
$V_\infty$ – asymptote values determined by means of various methods
$\beta$ – maximum calculated conversion

In Figure 3S below, the linearisation of the progression curve was shown for two cases of determination of $V_\infty$ from Table 1S.

Figure 3S. The comparison between linearisation of the progression curve using the parameters determined by nonlinear fitting (lower straight line) and after the reaction was completed by heating the mixture (top straight line)

The values of $V_\infty$ obtained iteratively and by nonlinear fitting are virtually the same. However, they differ significantly from the values obtained experimentally, which additionally lead to results with worse statistical characteristics (standard deviation and $R^2$). Thus, as you may notice, even a very good implementation of an experiment does not
guarantee that the value of $V_\infty$ will be experimentally determined accurately enough, whereas the values determined numerically provide virtually ideal fitting. It can therefore be assumed that the determined rate constants will also be closer to the real values.

1. **Analysis of the kinetics of sucrose hydrolysis**

In another laboratory experiment, students analysed the hydrolysis of sucrose whose results were shown in Table 3S.

**Table 3S.** The sample data on the progress of hydrolysis reaction of 10% sucrose solution catalysed with an acid whose concentration in the sample was 0.4 mol/L

| time [min] | the angle of rotation $\alpha$ |
|------------|-------------------------------|
| 0          | 13.05                         |
| 10         | 12.45                         |
| 20         | 11.9                          |
| 30         | 11.45                         |
| 40         | 11.05                         |
| 50         | 10.6                          |
| 60         | 10.1                          |
| 70         | 9.65                          |
| 80         | 9.2                           |
| 90         | 8.85                          |
| 100        | 8.35                          |
| 130        | 7.15                          |
| 160        | 6                             |
| 190        | 5                             |
| 210        | 4.15                          |
| 240        | 2.9                           |
| 270        | 2.25                          |
| 300        | 1.5                           |
| 330        | 0.75                          |
| 360        | 0.5                           |
| 390        | -0.85                         |
| 810        | -4.5                          |
**Figure 4S.** The experimental (points) progression curve and one calculated (line) on the basis of parameters determined iteratively

A fitting close to the proposed iterative method was also obtained by the nonlinear method.

**Table 4S.** The calculated and the experimentally determined values of $\alpha_\infty$ and their corresponding values of rate constants together with the statistical assessment (obtained for a 10% sucrose solution)

| Parameter | The method of determination of $\alpha_\infty$ |
|-----------|---------------------------------------------|
|           | nonlinear | iteratively | after heating | after 12.5 h |
| $\alpha_\infty$ = | -6.6064 | -5.963 | -4.55 | -4.55 |
| $k$ = | 0.002848 | 0.003218 | 0.00625 | 0.00625 |
| SDk = | 4.219E-05 | 3.28E-05 | 0.000484 | 0.000484 |
| $R^2$ = | 0.9956 | 0.9979 | 0.9928 | 0.9928 |
| $\beta$ = | 0.892566 | 0.924371 | 0.997151 | 0.997151 |

where:
- $k$ – observed reaction rate constant [1/min]
- SDk – standard deviation of the rate constant
- $R^2$ – coefficient of determination
- $\alpha_\infty$ – asymptote values determined using various methods
- $\beta$ – maximum calculated conversion

The results shown in Table 4S confirm the advantage of numerical methods of determining the kinetic parameters over the methods based on linearisation using the experimentally determined value of $\alpha_\infty$. As it can be seen, in the above case this is not due to too low conversion, since it does not differ significantly for all methods applied.

For the purpose of comparison, below are the results of the experiment which involved modifying some reaction parameters, i.e. the initial concentration of sucrose had been reduced two times and the measurement time for one of the samples (the non-heated one) had been extended to three days.
Table 5S. The sample data on the progress of inversion reaction of 5% sucrose solution catalysed with an acid whose concentration in the sample was 0.4 mol/L

| time [min] | the angle of rotation α |
|------------|-------------------------|
| 0          | 6.5                     |
| 10         | 6.25                    |
| 20         | 6                       |
| 30         | 5.75                    |
| 40         | 5.5                     |
| 50         | 5.35                    |
| 60         | 5.2                     |
| 70         | 5.05                    |
| 80         | 4.85                    |
| 90         | 4.65                    |
| 100        | 4.45                    |
| 110        | 4.25                    |
| 120        | 4                       |
| 150        | 3.3                     |
| 180        | 2.7                     |
| 210        | 2.5                     |
| 240        | 2.15                    |
| 270        | 1.65                    |
| 300        | 1.15                    |
| 330        | 1.05                    |
| 360        | 0.75                    |
| 1350       | -2                      |
| 1560       | -2.1                    |

Figure 5S. The experimental (points) progression curve and one calculated (line) on the basis of parameters determined iteratively
Table 6S. The calculated and the experimentally determined values of $\alpha_\infty$ and their corresponding values of rate constants together with the statistical assessment (obtained for a 5% sucrose solution)

| Parameter  | The method of determination of $\alpha_\infty$ |  |
|------------|---------------------------------------------|--|---|---|---|
|            | nonlinear | iteratively | after heating | after three days |
| $\alpha_\infty$ | -2.2026 | -2.192 | -2.15 | -2.85 |
| $k$         | 0.002826  | 0.002916 | 0.00319 | 0.00167 |
| SD$_k$      | 1.95e-5  | 1.92e-5  | 3.77e-5 | 6.62e-5 |
| R$^2$       | 0.999    | 0.999    | 0.997   | 0.968   |
| $\beta$     | 0.988    | 0.990    | 0.994   | 0.919   |

where:
- $k$ – observed reaction rate constant [1/min].
- SD$_k$ – standard deviation of the rate constant.
- R$^2$ – coefficient of determination.
- $\alpha_\infty$ – asymptote values determined using various methods.
- $\beta$ – maximum calculated conversion.

The results shown in Table 6S also confirm the advantage of numerical methods of determining the kinetic parameters over the methods based on the experimentally determined value of $\alpha_\infty$. The obtained values of rate constants (for the asymptotes determined numerically) are similar for both described cases (10% and 5% of sucrose). Of course, in the second case the reaction is slower and that is why it is more convenient to track it. Also, this is probably why the obtained values have better statistical characteristics. However, it should be noted that there is a negative influence of long storage time of the sample for the purpose of experimentally determining $\alpha_\infty$. The probable cause might be that the sample was not stored under sterile conditions.

Analysis of the kinetics of base hydrolysis of an ester- pseudo-first order reactions

The problem applies only to the pseudo-first order reaction, in which a corresponding excess of reagent(s) is required in relation to the one whose concentration changes generate a change in the measured signal. Of course, as much excess as possible should be used to control the course of the reaction. Due to the limited time of student classes, but also the limitations of the analytical method used, this excess may not be satisfactory at the very beginning of the reaction. However, since the conversion can be calculated beginning from any initial concentration value in this case, the measurement does not have to be started at the moment of mixing the reagents (this also generates disturbances at the beginning). Measurement can be started with a certain delay, which improves the ratio of the concentration of redundant reagents to that of the deficient reagent. Thus, the condition for recognising the reaction as a pseudo-first order process is better fulfilled.
The example was given in the table below:

|      | 0 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 |
|------|---|-----|-----|-----|-----|-----|-----|-----|
| C_{ester} | 0.04 | 0.032 | 0.033 | 0.034 | 0.035 | 0.036 | 0.037 | 0.038 |
| C_{OH} | 0.01 | 0.008 | 0.007 | 0.006 | 0.005 | 0.004 | 0.003 | 0.002 |
| ratio | 4.0 | 4.0 | 4.7 | 5.7 | 7.0 | 9.0 | 12.3 | 19.0 |

|      | 0 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 |
|------|---|-----|-----|-----|-----|-----|-----|-----|
| C_{ester} | 0.08 | 0.072 | 0.073 | 0.074 | 0.075 | 0.076 | 0.077 | 0.078 |
| C_{OH} | 0.01 | 0.008 | 0.007 | 0.006 | 0.005 | 0.004 | 0.003 | 0.002 |
| ratio | 8.0 | 9.0 | 10.4 | 12.3 | 15.0 | 19.0 | 25.7 | 39.0 |