

DETERMINATION OF KINETIC PARAMETERS OF THE CRYSTAL VIOLET REACTION WITH SODIUM HYDROXIDE APPLYING ABSORBANCE TECHNIQUE AND THE LAWS OF LAMBEERT-BEER AND ARRHENIUS

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ABSTRACT

A reaction widely used to test CSTR reactors is the reaction between crystal violet and sodium hydroxide, since crystal violet discolouration occurs in proportion to the reaction's progress (ATKINS, 2006; RANGEL, 1995). The present work has the objective of verifying first order kinetics and obtaining the kinetic parameters, such as rate constant, frequency factor and activation energy for the present reaction. A calibration curve was constructed, obeying the Lambert-Beer Law, so that it is possible to know the concentration in each time period of the reaction by the absorbance technique. All samples were analyzed at a wavelength of 595nm, due to providing a higher absorbance value. The results obtained were proportionality constant of $824,383 \text{ L mol}^{-1} \text{ cm}^{-1}$, activation energy of $57.44 \text{ kJ mol}^{-1}$ and frequency factor of $6.41 \cdot 10^{10} \text{ L mol}^{-1} \text{ min}^{-1}$. The rate constants obtained were 7.77, 12.05, 18.21 and 22.28 for temperatures of 30 °C, 35 °C, 40 °C and 45 °C respectively. The lowest R^2 value of the line adjustment was 0.9798, demonstrating reliability in the obtained results.

KEYWORDS: crystal violet, kinetic parameters, standard curve

DETERMINAÇÃO DE PARÂMETROS CINÉTICOS DA REAÇÃO DO CRISTAL VIOLETA COM O HIDRÓXIDO DE SÓDIO APLICANDO À TÉCNICA DA ABSORBÂNCIA E AS LEIS DE LAMBEERT-BEER E ARRHENIUS

RESUMO

Uma reação bastante utilizada a fim de testes em reatores do tipo CSTR é a reação entre cristal violeta e hidróxido de sódio, já que ocorre a descoloração do cristal violeta em proporção ao avanço da reação (ATKINS, 2006; RANGEL, 1995). O presente trabalho tem como objetivo a verificação da cinética de primeira ordem e obtenção dos parâmetros cinéticos, como a constante de velocidade, o fator de frequência e a energia de ativação para a presente reação. Construiu-se uma curva de calibração, obedecendo a Lei de Lambert-Beer, para que seja possível saber a concentração em cada período de tempo da reação por meio da técnica da absorbância. Todas as amostras foram analisadas a um comprimento de onda de 595nm, devido a fornecer um maior valor de absorbância. Os resultados obtidos foram: constante de proporcionalidade de $824.383 \text{ L mol}^{-1} \text{ cm}^{-1}$, Energia de Ativação de $57,44 \text{ kJ mol}^{-1}$ e fator de frequência de $6,41 \cdot 10^{10} \text{ L mol}^{-1} \text{ min}^{-1}$. As constantes de

velocidade obtidas foram de 7,77; 12,05; 18,21 e 22,28 para as temperaturas de 30 °C, 35 °C, 40 °C e 45 °C respectivamente. O menor valor de R^2 do ajuste da reta foi de 0,9798, demonstrando confiabilidade nos resultados obtidos.

PALAVRAS-CHAVE: cristal violeta, parâmetros cinéticos, curva padrão

INTRODUCTION

Crystal violet (gentian violet, methyl violet 10 B, scientifically named pararosaniline chloride) is a known antiseptic and antimycotic agent. It is the primary dye used in the Gram staining process, and perhaps the most important bacterial agent in use today. In addition, it is used in hospitals for the treatment of severe burns and other skin lesions and gums (FERREIRA et al., 2015; LI et al., 2016).

Crystal violet, of molecular formula $C_{25}H_{30}N_3Cl$, is an ionic compound that, in aqueous solution, dissociates into $C_{25}H_{30}N_3^+$ and Cl^- ions (GAUTAM et al., 2016). As a consequence of the electronic delocalization observed in the cation $C_{25}H_{30}N_3^+$ the solution shows the violet hue. In the presence of OH^- the $C_{25}H_{30}N_3^+$ species reacts giving a colorless carbinol, according to Figure 1: (CORSARO, 1964).

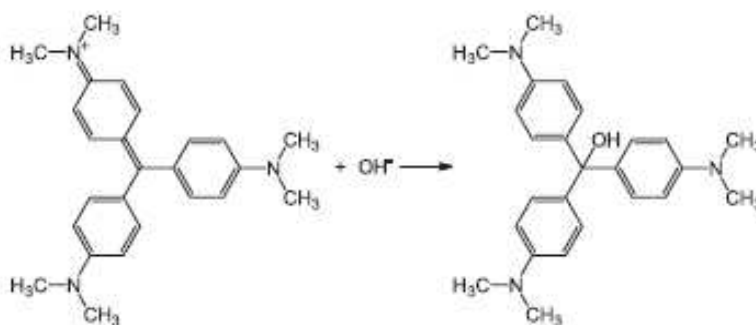


FIGURE 1. Reaction of the crystal violet with the hydroxide ion. Source: Corsaro (1964).

The fact that only the crystal violet absorbs in the visible region of the spectrum, with a band centered at 595 nm, allows spectrophotometry to be used in the visible region to study the kinetics of the reaction, mainly in reactors of the type CSTR, as can be seen in Figure 2: (DU et al., 2013).

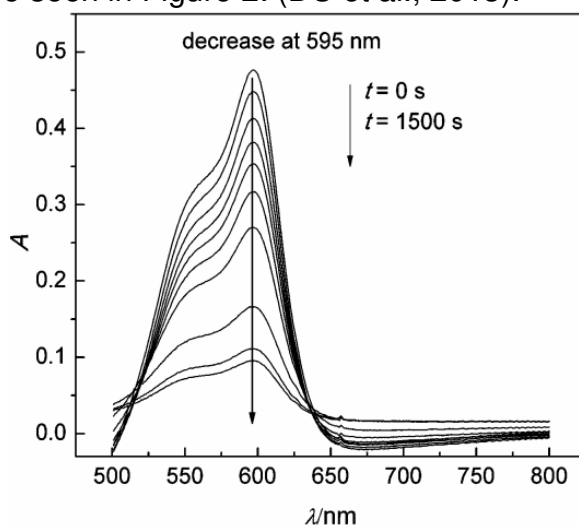


FIGURE 2. Variation of absorption spectrum with time for the reaction of crystal violet with hydroxide ion in the critical solution of 2-butoxyethanol + water at 319.16K. Source: DU et al. (2013).

A very common reactor in industrial processes is the CSTR (Continuous Stirred Tank Reactor) is a very common reactor in industrial processes. This reactor is used for liquid reagents, promoting the perfect mixing between them so that the reaction takes place in a more efficient way (CUI et al., 2016).

Spectrophotometry is an analytical technique that evaluates the ability of solutes to absorb light at specific wavelengths, as well as having high sensitivity and low cost of use (KAZEMI et al., 2016; LODEIRO et al., 2017). The Lambert-Beer Law relates the absorbance with concentration, the optical path (distance in which light traveled in the cuvette) and the constant of proportionality (found in this work). The law can be described by Equation 1 (MÂNTELE & DENIZ, 2017).

$$A = \epsilon b C \quad (1)$$

wherein: A = absorbance; ϵ = proportionality constant, units in $L \text{ mol}^{-1} \text{ cm}^{-1}$; B = distance from the optical path, units in cm; C = concentration of analyte, units in mol L^{-1} .

The velocity equation quantifies the rate variation of a reaction in relation to the concentrations of the species involved in it (LAIDLER, 1987). This is usually expressed in terms of the rate of consumption of a given reactant, or of appearance of a product, per unit of time. In the case of the reaction of addition of the hydroxide ion to the crystal violet, being a reaction involving two reactants, the equation of velocity is expressed by Equation 2 (CONCEIÇÃO & DIOGO, 2013):

$$-\frac{d[CV^+]}{dt} = k[CV^+]^\alpha [OH^-]^\beta \quad (2)$$

wherein: $[CV^+]$ and $[OH^-]$ the concentrations of crystal violet and hydroxide ion, respectively; α and β the partial orders corresponding to each substance, the order of reaction being $\alpha + \beta$; K is the reaction rate constant valid for a given temperature and ionic strength.

The order of a reaction can be fractional or zero and its determination is made by adjusting the parameters of the velocity equation with the experimental data. The order of reaction is not necessarily linked to the stoichiometric equation (ATKINS, 2006; SKOOG et al., 2007). If the initial concentration of the CV^+ reagent is small in relation to the OH^- , its fractional variation be greater than OH^- and the concentration of OH^- can be considered constant and equal to the initial value. Assuming that the reaction is first order with respect to CV^+ , there is Equation 3 (CONCEIÇÃO & DIOGO, 2013; YANG et al., 2017).

$$-\frac{d[CV^+]}{dt} = k'[CV^+] \quad (3)$$

Integrating and rearranging Equation 3 gives Equation 4.

$$\ln \frac{CV_0^+}{CV_t^+} = k't \quad (4)$$

wherein: CV_0^+ is the initial concentration of crystal violet; CV_t^+ is the concentration of crystal violet measured after elapsed time t.

If the graph of $\ln(CV_0^+ / CV_t^+)$ as a function of t is a straight line, it will confirm that the reaction is first order with respect to CV^+ , and the coefficient will determine the value of k'. Activation energy is the initial energy needed for a reaction to take place. The Arrhenius equation provides the basis for the relationship between the activation energy and the rate at which the reaction (ATKINS, 2006; SKOOG et al., 2007). From the Arrhenius equation, the activation energy (E_a) can be expressed by Equation 5.

$$E_a = -RT \ln\left(\frac{k}{A}\right) \quad (5)$$

wherein: A is the frequency factor for the reaction, R is the universal gas constant (8.314 J K⁻¹ mol⁻¹), and T is the temperature (in Kelvin).

Rearranging Equation 5 comes to Equation 6, which is best to determine the activation energy with experimental data (CANTU et al., 2014).

$$\ln k = -\frac{E_a}{R} \cdot \left(\frac{1}{T}\right) + \ln A \quad (6)$$

MATERIAL AND METHODS

Calibration curve

For the first experiment, in which the calibration curve was constructed, the following materials were required:

- Stock solution of crystal violet 3,525 x 10⁻⁵ mol L⁻¹;
- Test tubes;
- Acrylic cuvettes of 1 cm thickness;
- FEMTO spectrophotometer model 435.

The stock solution was diluted in volumetric flask, in the ratio of 1:40, using 5 ml of solution to 195 ml of water. According to Table 1, solutions were assembled in duplicate of violet solution using test tubes. These were shaken and their absorbances were measured in a spectrophotometer, at the wavelength of 595 nm, forming a calibration curve.

TABLE 1. Dilution of the crystal violet solution.

Tube nº	Crystal violet (ml)	Distilled water (ml)	Crystal violet concentration (mol L ⁻¹)	Tube nº	Crystal violet (ml)	Distilled water (ml)	Crystal violet concentration (mol L ⁻¹)
01	0.00	4.00	0.00E+00	12	2.20	1.80	4.85E-07
02	0.20	3.80	4.41E-08	13	2.40	1.60	5.29E-07
03	0.40	3.60	8.81E-08	14	2.60	1.40	5.73E-07
04	0.60	3.40	1.32E-07	15	2.80	1.20	6.17E-07
05	0.80	3.20	1.76E-07	16	3.00	1.00	6.61E-07
06	1.00	3.00	2.20E-07	17	3.20	0.80	7.05E-07
07	1.20	2.80	2.64E-07	18	3.40	0.60	7.49E-07
08	1.40	2.60	3.08E-07	19	3.60	0.40	7.93E-07
09	1.60	2.40	3.53E-07	20	3.80	0.20	8.37E-07
10	1.80	2.20	3.97E-07	21	4.00	0.00	8.81E-07
11	2.00	2.00	4.41E-07				

Care has been taken that the absorbance has values below 0.8 because the Lambert-Beer Law suffers significant deviations with absorbances greater than 1 (MÂNTELE & DENIZ, 2017).

Kinetics of the reaction

For the second experiment, in which the kinetics of the reaction was constructed, the following materials were required:

- Stock solution of crystal violet 3,525 x 10⁻⁵ mol L⁻¹;
- Sodium hydroxide solution 4 x 10⁻² mol L⁻¹;

- Stopwatch;
- Batch reactor (Figure 3);
- FEMTO spectrophotometer model 435.

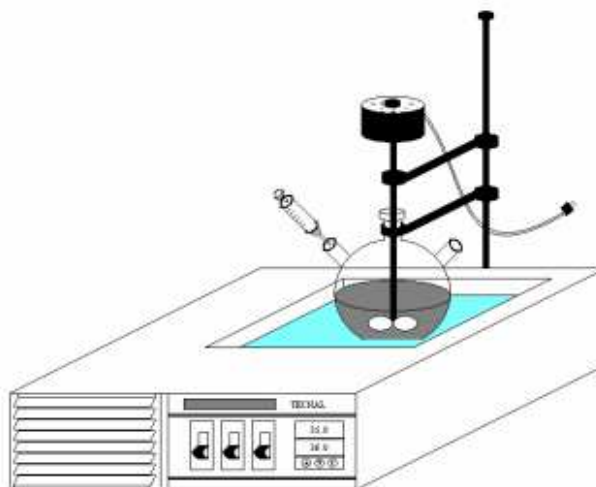


FIGURE 3. Experimental module for first order reaction.

In a volumetric flask, 150 ml of crystal violet solution was heated. Simultaneously, 150 ml of sodium hydroxide were also heated in a three-necked flask (reactor). Both solutions were in a bath at a temperature of 30 °C. When the temperature of both solutions had their temperatures stabilized at 30 °C, the crystal violet solution was added to the sodium hydroxide solution. Immediately after mixing, a 4 ml sample was withdrawn, and this was cooled in a cold water bath to stop the reaction and read on the spectrophotometer at the wavelength of 595 nm. From this sample, at each defined interval of time a new sample of 4 ml was withdrawn, cooled and read in the spectrophotometer. Throughout the experiment the temperatures in the reactor and in the bath were monitored. The procedure described above was repeated for temperatures of 35, 40 and 45 °C.

RESULTS AND DISCUSSIONS

Calibration curve

The values obtained for the absorbances (Abs.) are listed in Table 2. All measurements were performed in duplicate.

TABLE 2. Measured Absorbances.

Tube n°	Abs. 1	Abs. 2	Average Abs.	Tube n°	Abs. 1	Abs. 2	Average Abs.
01	0.000	0.000	0.000	12	0.405	0.394	0.400
02	0.010	0.011	0.011	13	0.432	0.428	0.430
03	0.054	0.052	0.053	14	0.488	0.450	0.469
04	0.065	0.074	0.070	15	0.528	0.495	0.512
05	0.127	0.121	0.124	16	0.566	0.575	0.571
06	0.154	0.146	0.150	17	0.578	0.589	0.584
07	0.199	0.169	0.184	18	0.584	0.597	0.591
08	0.184	0.202	0.193	19	0.654	0.667	0.661
09	0.249	0.245	0.247	20	0.727	0.744	0.736
10	0.332	0.315	0.324	21	0.764	0.753	0.759
11	0.339	0.358	0.349				

From the mean absorbance values, a plot of absorbance per concentration was constructed, as shown in Figure 4.

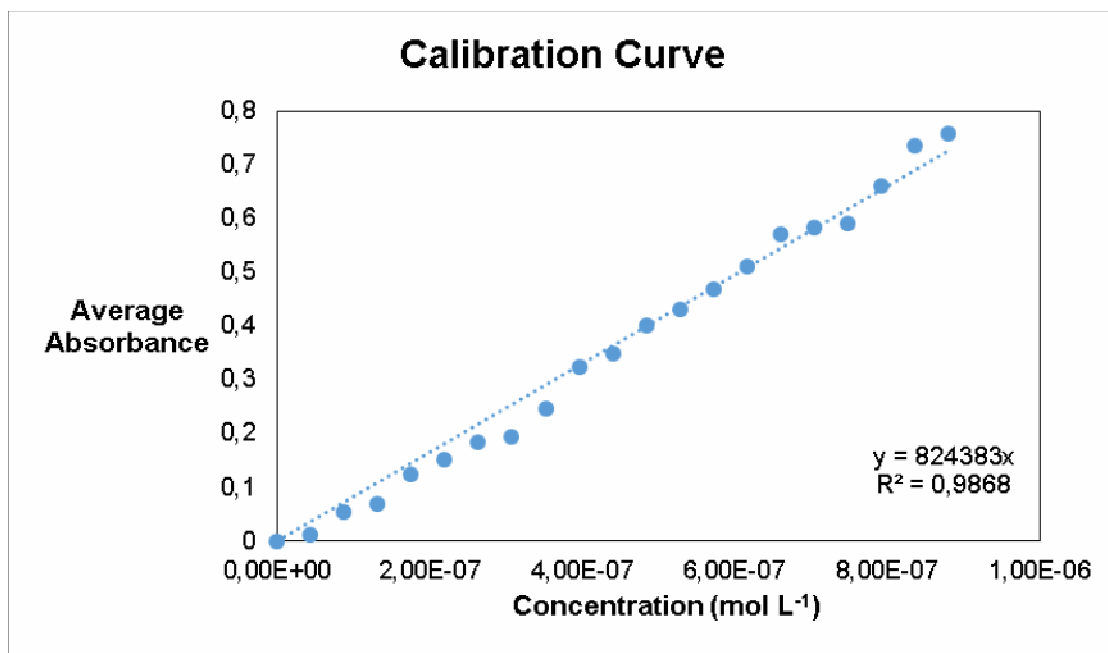


FIGURE 4. Calibration curve (Absorbance x Concentration) with wavelength = 595 nm.

The optical path is 1cm which is the thickness of the bucket used. The equation found by the graph gives us the value of the proportionality constant (824,383 L mol⁻¹ cm⁻¹). By the Law of Lambert-Beer obtains Equation 7:

$$A = 824383bc \quad (7)$$

Kinetics of the reaction

The values obtained for the absorbances as a function of time are listed in Table 3 for each temperature studied.

TABLE 3. Absorbances measured.

t (min)	30 °C		35 °C		40 °C		45 °C	
	Abs.	$\ln(CV_0^+ / CV_t^+)$	Abs.	$\ln(CV_0^+ / CV_t^+)$	Abs.	$\ln(CV_0^+ / CV_t^+)$	Abs.	$\ln(CV_0^+ / CV_t^+)$
0	0.519	0	0.440	0	0.610	0	0.400	0
0.5	-	-	0.318	0.325	0.410	0.397	0.257	0.442
1.0	0.415	0.224	-	-	0.270	0.815	0.143	1.029
1.5	-	-	0.185	0.866	0.178	1.232	0.095	1.438
2.0	0.280	0.617	-	-	0.119	1.634	0.057	1.948
2.5	-	-	0.116	1.333	0.092	1.892	0.040	2.303
3.0	0.200	0.954	0.094	1.543	0.066	2.224	0.028	2.659
3.5	-	-	0.079	1.717	0.051	2.482	0.022	2.900
4.0	0.152	1.228	0.062	1.960	0.032	2.948	-	-
4.5	-	-	0.053	2.116	0.026	3.155	-	-
5.0	0.115	1.507	0.047	2.237	0.017	3.580	-	-
6.0	0.081	1.857	-	-	-	-	-	-
7.0	0.063	2.109	-	-	-	-	-	-
8.0	0.039	2.588	-	-	-	-	-	-
9.0	0.030	2.851	-	-	-	-	-	-
10.0	0.023	3.116	-	-	-	-	-	-
11.0	0.018	3.362	-	-	-	-	-	-

Figure 5 shows the results of the experiment at the different temperatures.

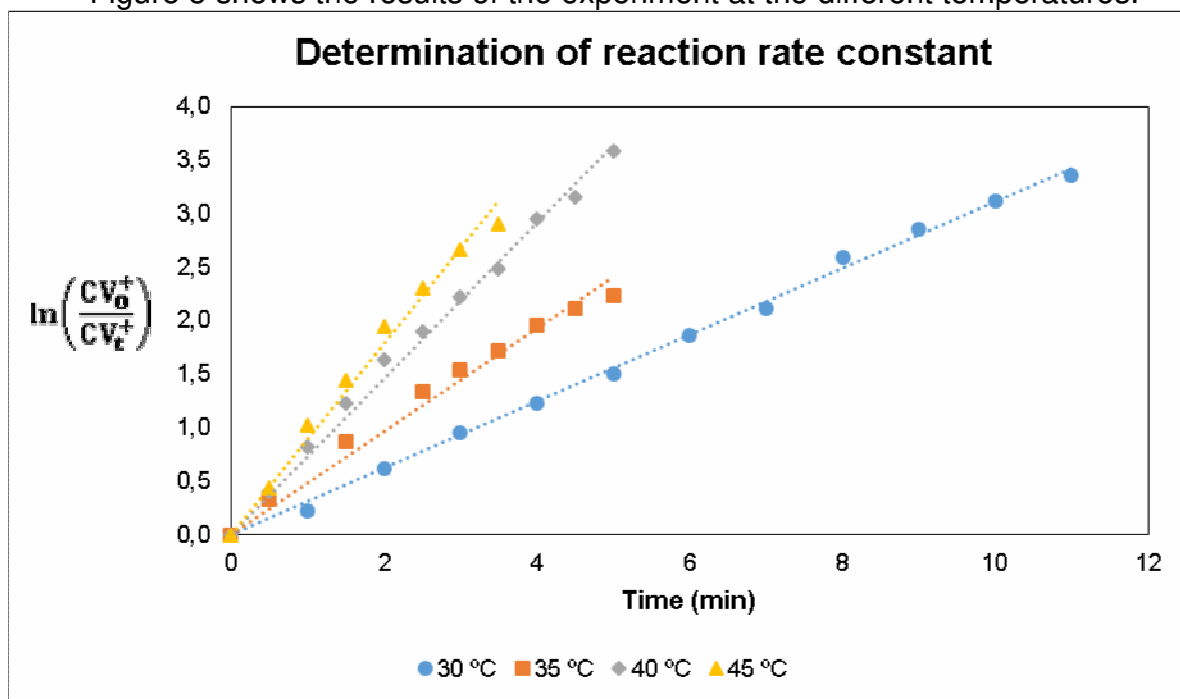


FIGURE 5. Graph with different curves of the experiments at different temperatures.

By means of the angular coefficients of each line was obtained the pseudo-first order reaction rate constants (k'), which are written together with respective values of the reaction rate constant (k) and the regression determination coefficients Linear (R^2) in Table 4.

TABLE 4. R^2 , k' and k values of each temperature.

Temperature (°C)	R^2	k' (min ⁻¹)	$k = k'/C_{OH}^*$ (L mol ⁻¹ min ⁻¹)
30	0.9978	0.3106	7.77
35	0.9824	0.4820	12.05
40	0.9933	0.7284	18.21
45	0.9856	0.8911	22.28

* Where $C_{OH} = 0.04 \text{ mol L}^{-1}$

When plotting $\ln(k) \times 1/T$, both the activation energy of the reaction and its frequency factor are obtained due to Equation 6. Table 5 shows the values used to make the graph of Figure 6.

TABLE 5. Data adjusted to the Arrhenius equation of the natural logarithm of the velocity constant as a function of the inverse of the temperature.

Temperature ⁻¹ (Kelvin ⁻¹)	$\ln k$
3.30E-03	2.0496
3.25E-03	2.4891
3.19E-03	2.9020
3.14E-03	3.1036

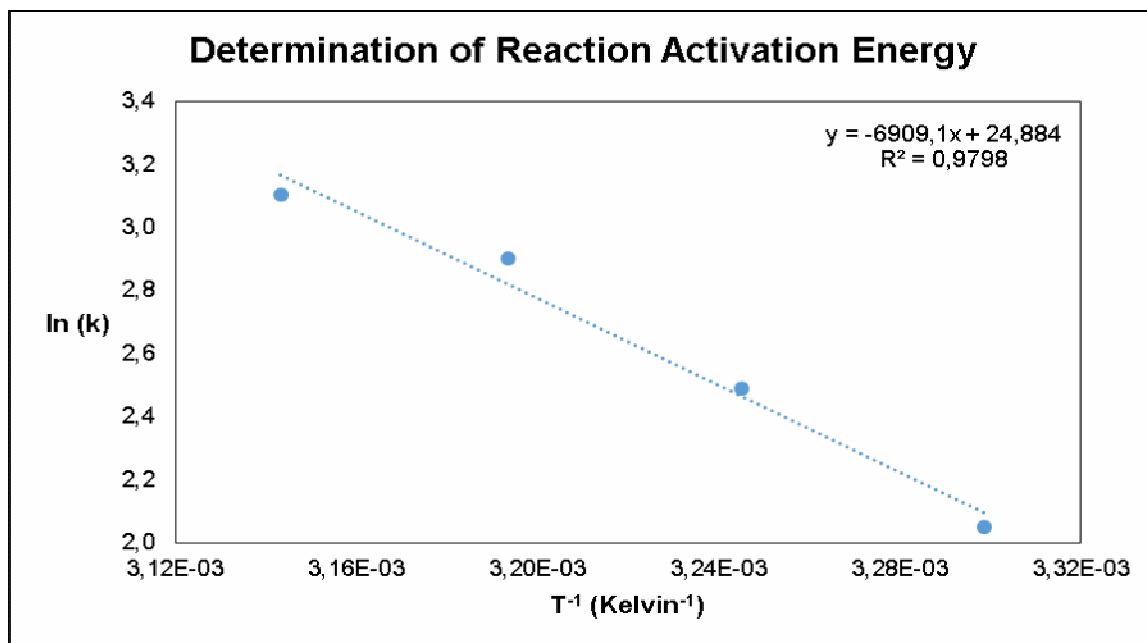


FIGURE 6. Graph of $\ln(k) \times 1/T$ for the determination of the activation energy and the frequency factor.

By means of Equation 6, arrive at:

$$\ln A = 24.884 \rightarrow A = 6.41 \cdot 10^{10} \text{ L mol}^{-1} \text{ min}^{-1}$$

$$-\frac{E_a}{R} = 6909.1 \rightarrow E_a = 57.44 \text{ kJ mol}^{-1}$$

As the coefficient of determination of linear regression gave a value of 0.9798 for the Arrhenius Equation, the values obtained here demonstrate good reliability. As the frequency factor value (A) was obtained by exponential linear coefficient of the line, this value is what most shows variations depending on the equation of the line obtained.

CONCLUSIONS

By means of a curve with 21 experimental points in duplicate, the standard curve of the crystal violet was plotted, with a R^2 of 0.9868, proving that the curve is correctly fitted to the Lambert-Beer law. With the obtained value of the constant of proportionality of $824,383 \text{ L mol}^{-1} \text{ cm}^{-1}$, it is possible to carry out studies in the reactional analysis.

The curves of determination of the kinetic constant had values of 7.77, 12.05, 18.21 and $22.28 \text{ L mol}^{-1} \text{ cm}^{-1}$ for the temperatures of 30, 35, 40 and $45 \text{ }^\circ\text{C}$, respectively. These values obeyed the first order reaction equation, since the lowest R^2 value was 0.9824.

By means of the values of the speed constants, he found the frequency factor value of $6.41 \cdot 10^{10} \text{ L mol}^{-1} \text{ min}^{-1}$ and the activation energy of $77.44 \text{ kJ mol}^{-1}$. As the R^2 value was 0.9798, the data adjusted very well to the Arrhenius equation, guaranteeing a reliable result.

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