Journal of
Emerging Investigators

The Cohesiveness of the Oscillating Belousov-Zhabotinsky Reaction

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Summary

The Oscillating Belousov-Zhabotinsky (B-Z) Reaction is a chemical reaction initially studied by Russian military officer Belousov. Oscillating reactions are characterized by a change in ion concentration overtime, a perpetual back and forth flow between two contrasting solutions. Numerous mechanisms have been proposed to underlie the B-Z reaction. The model known as the Oregonator provides a simplified mechanism to reach the oscillating state. In order to interrogate the mechanisms that enable the B-Z reaction, we performed an experiment using the Oregonator. The data was collected from the reaction at four different temperatures, 10, 22, 37, and 50°C. A Markovian Analysis was used to interpret the 300 pieces of data that were collected. The change in conductivity was measured in between each sample and the calculations were imputed into a square matrix. When the matrix was squared in each trial, we found that there were two transition states between the original and steady matrices, representing the intermediate reactions between the oscillations. These findings were unique because the transition matrices have never been analyzed using change in conductivity and Markovian sequencing. From the steady matrix at each temperature, the probability of "hopping" between different changes in conductivity was determined in the long-term analysis of the oscillations. These values were also compared to determine temperature's effect on the cohesiveness of the oscillating B-Z reaction. The findings of this study are important to consider when applying the reaction into polymer gels, which mimic the pulsing motions of organs in the circulatory system. Understanding the oscillations of the B-Z reaction can help researchers better understand the movements of the polymer gel overtime.

Received: May 16, 2018; **Accepted:** August 17, 2018; **Published:** December 18, 2018

Introduction

The oscillating Belousov-Zhabotinsky (B-Z) reaction, which is characterized by the appearance and disappearance of a certain element in a recurring cycle, was originally discovered by Boris Pavlovich Belousov in a toxicology lab in the Soviet Ministry of Health. Later, the reaction was improved upon by graduate student Anatol Zhabotinsky, who gave the B-Z reaction its name (1). Since then, the oscillating B-Z reaction has been relatively understudied, and not much is understood about the "chaos" of the oscillations. The purpose of this research was to study the cohesiveness of the oscillating B-Z reaction in order to understand this reaction as it is applied to polymer gels. Cohesiveness is a measure of continuity that will predict how the oscillations will act in the long run and if the oscillations and transition states will continue over time.

Many people compare the B-Z reaction to a dynamic equilibrium system; however, oscillation is very different from equilibrium. The general knowledge of oscillating reactions can be applied to specific research on the oscillating B-Z reaction. Oscillating reactions are characterized by the change in ion concentration over time. As the reaction progresses, ions are produced and consumed through dissociation and association of chemical components. Conductivity is an ideal way to collect data from this reaction due to this change in ion concentration.

The B-Z reaction can be recreated using many different combinations of chemicals; however, the Oregonator mechanism is considered the simplest model of this reaction because it uses easily attainable chemicals (6). With the Oregonator mechanism, the oscillations observed are solutions of two different colors, beginning with an amber color due to the formation of bromine. The second part of the oscillation reveals a colorless solution, in which the consumption of bromine by malonic acid removes the amber color. The solution continually moves back and forth between colorless and amber.

Some research has been conducted specifically on the B-Z reaction. The reaction's oscillations have been analyzed in terms of chemical dynamics, reaction rates, and rate constants (7). In addition, the reaction has

	-10	0	10	total
-10	0 P (-10|-10) 0.00	27 P(0|-10) 0.614	17 P(10|-10) 0.386	44
0	28 P(-10|0) 0.130	167 P(0|0) 0.773	21 P(10|0) 0.0972	216
10	15 P(-10|10) 0.395	21 P(0|10) 0.553	2 P(10|10) 0.0226	38

Table 1a: Transition State

0.232	0.688	0.0800
0.139	0.731	0.130
0.0927	0.699	0.209

Table 1b: Transition State

0.157	0.719	0.125
0.146	0.721	0.134
0.138	0.721	0.142

Table 1c: Steady State

0.147	0.721	0.134
0.147	0.721	0.134
0.147	0.721	0.134

Table 1: Markovian Matrix Analysis of the data in the 10 degrees Celsius trial.

	-10	0	10	20	total
-10	1 P (-10|-10) 0.0256	30 P(0|-10) 0.769	8 P(10|-10) 0.205	0 P(20|-10) 0.00	39
0	32 P(-10|0) 0.135	190 P(0|0) 0.802	13 P(10|0) 0.0549	2 P(20|0) 0.00844	237
10	5 P(-10|10) 0.250	15 P(0|10) 0.750	0 P(10|10) 0.00	0 P(20|10) 0.00	20
20	2 P(-10|20) 1.00	0 P(0|20) 0.00	0 P(10|20) 0.00	0 P(20|20) 0.00	2

Table 2a: Transition State

0.156	0.790	0.0475	0.00650
0.134	0.788	0.0717	0.00677
0.108	0.794	0.0924	0.00633
0.0256	0.769	0.205	0.00

Table 2b: Transition State

0.135	0.789	0.0698	0.00666
0.134	0.789	0.0789	0.00666
0.133	0.789	0.0719	0.00666
0.129	0.789	0.0753	0.00666

Table 2c: Steady State

0.134	0.789	0.0709	0.00666
0.134	0.789	0.0709	0.00666
0.134	0.789	0.0709	0.00666
0.134	0.789	0.0709	0.00666

Table 2: Markovian Matrix Analysis of the data in the 22 degrees Celsius trial.

been modeled both theoretically and computationally using the Oregonator mechanism (8). These studies are based on the chaos theory of the B-Z reaction, or the hypothesis that the oscillations are random and erratic, and have focused on further analyzing this complex series of oscillating reactions as we have. However, one major gap in previous research relates to predicting how the oscillations will occur over time. Our study on the oscillating B-Z reaction aims to fill this gap by studying cohesiveness and predicting long-term chemical reactions using The Markovian sequencing method.

A Markov sequence chain calculates the probability of "hopping" from one state to another (9). Markov sequencing can be used to predict conditions in a random system and has been used by past researchers to predict random time delays in Nonlinear Network Control Systems (NCSs) (10). Markov sequencing has also been employed by researchers in the past to predict

	-10	0	10	20	total
-10	1 P (-10l-10) 0.0303	26 P(0l-10) 0.789	6 P(10l-10) 0.182	0 P(20l-10) 0.00	33
0	21 P(-10l0) 0.0913	186 P(0l0) 0.809	22 P(10l0) 0.0957	1 P(20l0) 0.00435	230
10	11 P(-10l10) 0.333	17 P(0l10) 0.515	4 P(10l10) 0.121	1 P(20l10) 0.0303	33
20	1 P(-10l20) 0.500	1 P(0l20) 0.500	0 P(10l20) 0.00	0 P(20l20) 0.00	2

Table 3a: Transition State

0.134	0.756	0.103	0.00895
0.111	0.778	0.106	0.00642
0.113	0.757	0.125	0.00591
0.0608	0.799	0.139	0.00218

Table 3b: Transition State

0.114	0.774	0.108	0.00668
0.113	0.774	0.108	0.00662
0.113	0.773	0.188	0.00661
0.112	0.774	0.180	0.00665

Table 3c: Steady State

0.113	0.775	0.109	0.00664
0.113	0.775	0.109	0.00664
0.113	0.775	0.109	0.00664
0.113	0.775	0.109	0.00664

Table 3: Markovian Matrix Analysis of the data in the 37 degrees Celsius trial.

	-10	0	10	total
-10	0 P (-10l-10) 0.00	15 P(0l-10) 0.789	4 P(10l-10) 0.211	19
0	11 P(-10l0) 0.0418	241 P(0l0) 0.916	11 P(10l0) 0.0418	263
10	9 P(-10l10) 0.563	6 P(0l10) 0.375	1 P(10l10) 0.0625	16

Table 4a: Transition State

0.152	0.802	0.0462
0.0618	0.888	0.0497
0.509	0.811	0.138

Table 4b: Transition State

0.0750	0.871	0.0533
0.0668	0.878	0.539
0.0649	0.873	0.618

Table 4c: Steady State

0.0672	0.876	0.0542
0.0671	0.876	0.0542
0.0672	0.877	0.0543

Table 4: Markovian Matrix Analysis of the data in the 50 degrees Celsius trial.

transmembrane protein topology with an application to complete genomes (11). These chains are often referred to as hidden Markov Models, a formal foundation for making probabilistic models used most often in computational biology (12). Using this method, Markov sequencing can be used to determine the cohesiveness of the oscillating B-Z reaction. It is hypothesized that the oscillating B-Z reaction will not be cohesive.

Results

The purpose of this study was to understand the cohesiveness of the oscillating B-Z reaction in order to apply it to self-oscillating polymer gels. We hypothesized that the oscillating B-Z reaction will not be cohesive. The Oscillating B-Z reaction was performed at four different temperatures, and conductivity was measured throughout each of these trials. The change in conductivity was calculated between each value and the values were tallies into a markovian matrix. The results are as follows: The conductivity of the B-Z reaction measured at 10°C over a period of 200 seconds and the change in conductivity between every two pieces of data was recorded in each trial. The original matrix represents the original probability of hopping from one value to the other (Table 1). For example, the box in the upper left corner shows that for the 10 degree Celsius trial there is a zero percent chance if hopping from a change in conductivity of negative 10 to negative 10. The matrix is squared until it reaches a steady state, where all of the values in each column of the matrix are equal. Squaring the original matrix revealed two transition states and a steady state matrix. Following the Markovian method, the table was squared until all data values in each column was equal known as the steady state (Table 1c). The two intermediate matrices are called transition matrices (Tables 1a and 1b), they are intermediate matrices found in the process of obtaining the steady state matrix (1c). The same process was followed for temperature trials at 22, 37, and 50 degrees Celsius (Tables 2, 3, and 4).

Discussion

The oscillating B-Z reaction is a relatively understudied chemical reaction. The cohesiveness of the reaction shows how the oscillations will act in the long run, i.e. whether they will remain the same or change over time. The purpose of this research was to study the cohesiveness of the oscillating B-Z reaction to understand this reaction, as this information can then be applied to polymer gels to make them self-oscillating.

The results of this study support the hypothesis that the oscillating B-Z reaction is not cohesive. Tables 1, 2, 3, and 4 of the results section represent the Markovian matrices for all four trials of the reaction. When the matrices were squared, two transition states were revealed before the matrix reached its steady state, where every value in each column coincides. The more transition states in a matrix, the less cohesive the reaction is. This demonstrates that the oscillating B-Z reaction is not very cohesive because all four temperature trials revealed only two transition states, despite the differences in actual conductivity values. Therefore, the results of this study also provide evidence that the cohesiveness of the B-Z reaction is not affected by temperature.

This research is important because the oscillating B-Z reaction can be applied to polymer gels, making them self-oscillating. The B-Z reaction is recognized as the chemical model for understanding autonomous phenomena in biological systems (2). The gel uses the oxidation of malonic acid in the B-Z reaction to generate the swelling and deswelling motions. These oscillating behaviors can be modified based on the physical construction of the gel. The self-oscillating gels have been found to mimic the muscles of the intestine and capillary veins, when arranged in a tubular shape. The gel systems demonstrate rhythmic pulses in mechanical motion like that of a heartbeat (3). Few laboratories have begun to create this novel type of gel. The gel uses a specific design that enables the researcher to control the self-oscillating behaviors (4). Researchers are considering ways to use the polymer gel as an implant in a human patient, so it is important that the reaction be sustainable when it performs a vital function in the body. In future research, we hope that a prototype can be developed more like the movements of the heart muscle for use in the fields of polymer science, materials science, physical chemistry, robotics, theoretical simulation, and biophysics. This will connect the B-Z reaction to a much broader range of disciplines than chemistry alone (5).

Other researchers have analyzed different chemical processes occurring in this reaction; however, no past studies have analyzed cohesiveness. This type of chemical oscillator must occur far from equilibrium to ensure that the Gibbs's free energy is large and negative, allowing it to be a spontaneous reaction (13). Our results prove that the reaction does not require activation energy as long as the chemical concentrations begin far from equilibrium. However, as it approaches equilibrium, the reaction slows, and the switch between amber and colorless solutions is not as fast as when the reaction began. This shows that the reaction is not cohesive, the reaction does not proceed in the same manner with which it began. The reaction has been further analyzed in terms of intermittent reactions in between the oscillations (14). This study relates to the transition matrices that were revealed in my research, showing the probability of hopping from conductivity states during the intermediate reactions.

This research produced significant results; however, there are a few limitations. The data was collected from a model of the B-Z reactions called the Oregonator mechanism because it is composed of chemicals that are safe and can be used outside of a professional laboratory setting. There are other proposed mechanisms of this reaction that can be performed in a professional setting. Analyzing the other forms of the reaction could provide more comprehensive results. The conclusions made in this study apply only to the Oscillating B-Z Reaction under the conditions tested. In addition, this research studied the B-Z reaction itself, not its application of the reaction to polymer gels because they are not easily accessible. Possible sources of error throughout this experiment should also be considered as a limitation. The chemicals we used were stored over a period of three months, which may have contributed to slight inaccuracies and errors in measurement. Finally, the results of this reaction can only be applied to the B-Z reaction and not to other oscillating reversible reactions such as the Haber process.

Methods

The oscillating B-Z reaction and Markovian analysis were conducted in a South Florida High School chemistry lab. The reaction was performed multiple times over the course of three months. To create the reaction, water, sulfuric acid, malonic acid, potassium bromate, and manganese sulfate were mixed as stated in the Oregonator mechanism (15). First, 75 mL of deionized water were poured into a 150-mL beaker, which was placed on a heat plate with a stirrer. Then, 7.5 mL of concentrated sulfuric acid was added to the water. A conductivity probe was placed into the reaction solution and was set to collect conductivity data as a function of time, recording a sample of data in μS every tenth of a second for three minutes. Next, 0.9 g of solid malonic acid and 0.8 g of solid potassium bromate were added to the solution. Finally, 0.18 g of solid manganese sulfate was stirred into the above solution, which caused the oscillations to begin. The reaction was performed using the specific procedures explained above to follow the Oregonator mechanism, the most accessible and reproducible form of the oscillating B-Z reaction.

The oscillations are caused by changes in ion concentrations, which were measured as conductivity. Conductivity is the measure of ions that can conduct electricity in a solution. The reaction was repeated at four different temperatures: 10, 22, 37, and 50°C . For the 10°C trial, the beaker was placed into a bucket of ice and the temperature was measured with a thermometer to make sure it remained at 10°C . The 22°C trial was performed at room temperature. For the 37°C and 50°C trials, a heat plate was used at different settings to regulate the temperature of the solution. The different trials were conducted to see the effect of temperature on the B-Z reaction, helping to apply the results of the study into self-oscillating polymer gels, which are created to be transplanted into the body at 37°C. Once the reaction was completed, the 300 pieces of data collected per trial were used for the Markovian analysis. The data recorded was graphed electronically and analyzed using Markov sequence chains. The sequence chain can be transferred into a matrix, called the Markov transition matrix, showing the original probability values of data recorded. Squaring the matrix allows us to analyze the data for the next generation, and the matrix will be squared until all values in a single column coincide, revealing transition matrices. The revealed transition matrices represent the intermediate reactions of the B-Z oscillations. The number of transition matrices revealed signifies how cohesive the reaction is and allows the values in the intermediate reactions to be predicted. To perform the Markovian analysis, the change in conductivity between each sample of data was calculated for every trial performed. The change in conductivity values were all one of four values: -10, 0, 10, and 20. The values were tallied in a square matrix. For example, if the first change in conductivity value was 10 and the second value was 0, a tally would be placed in the box where the row labeled 10 and the column labeled 0 meet. Next, the probability was calculated by dividing the tallied number in each box by the total tally of each row. The probability values were put into a square matrix and the matrix was squared until it reached the steady state, where all the values in each column coincide.

References

1. Kiprijanov, Konstantin S. “Chaos and Beauty in a Beaker: The Early History of the Belousov-Zhabotinsky Reaction.” Annalen Der Physik, vol. 528, no. 3-4, 2016, pp. 233–237. doi:10.1002/andp.201600025.
2. Yoshida, Ryo. “Design of self-oscillating gels and application to biomimetic actuators.”Sensors, vol. 10, no. 3, 2010, pp. 1810-1822
3. Yoshida, Ryo; Ichijo, Hisao; Hakuta, Toshikatsu; & Yamaguchi, Tomohiko. “Self□oscillating swelling and deswelling of polymer gels.” Macromolecular rapid communications, vol. 16, no. 4, 1995, pp. 305-310
4. Yoshida, Ryo. “Self□Oscillating Polymer Gels. Supramolecular Soft Matter: Applications in Materials and Organic Electronics.” 2011, pp. 237-253.
5. Yoshida, Ryo, & Ueki, Takeshi. “Evolution of self-oscillating polymer gels as autonomous polymer systems.” NPG Asia Materials, vol. 6, no. 6, 2014. doi:10.1038/am.2014.32
6. Español, Malena I., & Rotstein, Horacio G. “Complex mixed-mode oscillatory patterns in a periodically forced excitable Belousov-Zhabotinsky reaction model.” Chaos, vol. 25, no. 6, 2015. doi:10.1063/1.4922715
7. Field, Richard J. “Chaos in the Belousov-Zhabotinsky reaction.” Modern Physics Letters B, vol. 29, no. 34, 2015. doi:10.1142/S021798491530015X
8. Yashin, Victor V., & Balazs, Anna C. “Theoretical and computational modeling of self-oscillating polymer gels.” Journal Of Chemical Physics, vol. 126, no. 12, 2007, pp. 124707 doi:10.1063/1.2672951
9. Rabiner, Lawrence R., & Juang, Biing H. “An introduction to hidden Markov models.” IEEE ASSP Magazine, vol. 3, no. 1, 1986, pp. 4-16.
10. Wang, Yanfeng; Wang, Peiliang; Li, Zuxin; & Chen, Huiying. “Observer-Based Controller Design for a

Class of Nonlinear Networked Control Systems with Random Time-Delays Modeled by Markov Chains." Journal Of Control Science & Engineering, 2017, pp. 1-13. doi:10.1155/2017/1523825

11. Krogh, Anders; Larsson, Björn; Von Heijne, Gunnar; & Sonnhammer, Erik L."Predicting transmembrane protein topology with a hidden Markov model: application to complete genomes." Journal of Molecular Biology, vol. 305, no. 3, 2001, pp. 567-580.
12. Eddy, Sean R. "What is a hidden Markov model?." Nature biotechnology, vol. 22, no. 10, 2004, pp. 1315-1316. doi:10.1038/nbt1004-1315
13. Das, Kuheli; Sahoo, Parashuram; & Murali, N. "Studies on oscillating chemical reaction in Cu(II)-catalyzed thiocyanate-hydrogen peroxide-NaOH system using pulsating sensor." International Journal Of Chemical Kinetics, vol. 45, no. 1, 2013, pp. 19-29. doi:10.1002/kin.20738
14. Pomeau, Yves; Roux, Justus C; Rossi, Andrea; Bachelart, S., & Vidal, C. "Intermittent behaviour in the Belousov-Zhabotinsky reaction." Journal de Physique Lettres, vol. 42, no. 13, 1981, pp. 271-273
15. R. J. Field, E. Körös and R. M. Noyes. "Oscillations in Chemical Systems II. Thorough analysis of temporal oscillations in the Ce-BrO3- - malonic acid system." Journal of the American Chemical Society, 94: 8649-64, 1972.