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Influence of Heavy Water on Waves and Oscillations in the Belousov-Zhabotinsky Reaction

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1. Introduction

Excitable media allow excitation waves to travel through them, which play an important role in a variety of natural processes, in physics, chemistry and live-sciences. (Sagues & Epstein, 2003; Tabony, 2006). By far the best understood model system for all these processes is the Belousov-Zhabotinsky (BZ) reaction (Belousov, 1959; Zaitkin & Zhabotinsky, 1970). This oscillating chemical reaction, among others, exhibits propagation of two-dimensional waves in thin layers of reaction solution (Luengviriya et al., 2006) or in gels (Yamaguchi et al., 2006), typically at velocities of some millimeter per minute. Also, in a stirred bulk solution, regular oscillations in time can be observed (Dolzmann et al., 2007).

From the beginning a variety of detailed kinetic models have been constructed to explain the oscillatory behavior of the bulk BZ reaction. The first and simplest is known as the FKN-model (Field et al., 1972), which involves 18 elementary steps and 21 chemical species. It can be simplified, however, assuming three key species: HBrO_2 as exchange intermediate, Br^- as control intermediate and Mox , i.e. the oxidized form of the catalyst, as regeneration intermediate. Later other, sometimes much more complex model have been composed.

According to the propagation of waves in thin layers of excitable medium, similar theories have been build up which, however, have to include diffusion of the involved species.

The oscillating BZ-reaction is expected to be a useful model for biological fluctuations (i.e. Winfree, 1987). Here it is dogma that the substitution of normal (light) water by heavy-water slows down every biological rhythm and process. The influence of deuterated compounds on the global kinetics of BZ reaction in stirred bulk systems was discussed by Karavaev et al. for Ru-catalyzed systems (1986). It was found that the substitution of H_2O by D_2O as solvent caused a complete suppression of the oscillating regime. In other studies (Hsu & Jwo, 1999; Rossi et al., 2007, 2009) an increase induction period of the oscillations was found. In any case a deuteration reaction and the bromation of the organic compound of the system in the theoretical framework can be made responsible for the effects described. This means, putting the effects into the rate constants.

Not very much is known about the effects of heavy water on propagating waves of the BZ-reaction. Theoretically also a slowing down of the wave fronts might be predicted, but in

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addition to the situation of the oscillating system, here diffusion of the involved species has to be taken into account, and this is lower in heavy water due to the increased viscosity (see materials section).

First we have done some more simple experiments with an oscillating BZ-reaction using normal-water and heavy-water, and then have investigated the behaviour of propagating waves in BZ-systems in more detail.

2. Materials and methods

2.1 General

All salts and solvents including heavy water were obtained from Sigma at a quality of p.a. or better. Normal water was from a double laboratory distillery.

Wave propagation experiments in fluids and gels were done in Petri-dishes (35mm and 100mm diameter), bulk oscillation experiments were done in laboratory beakers with a volume of 500ml.

In the wave-propagation experiments, the Petri-dishes were fixed on a light table (white light), a colour video-camera was mounted over them and the video traces were recorded on a computer using the proper hardware. In some cases a blue filter between light panel and Petri-dish was used to enhance the contrast.

In the bulk-oscillation experiments the beaker with the solution was fixed on a laboratory stirrer/heater. On one side of the beaker a blue LED (480nm) was mounted, on the other side a photomultiplier. The data from the photomultiplier (intensity of transmitted light) were stored on a computer using the proper A/D-converter and software. More details about the set-ups used have been published previously (Hanke, 1999; Dolzmann et al., 2007).

In all procedures described below, experiments were done identically for D₂O and H₂O. D₂O was used in all steps of the D₂O experiments, thus the remaining concentration of H₂O in the D₂O experiments was neglectable (far below 1% according to our calculations). To have the necessary physico-chemical information available, the data for normal- and heavy water are summarized in table 1.

	D ₂ O	H ₂ O
Freezing point (°C)	3.8	0.0
Boiling point (°C)	101.4	100.0
Density (at 20°C, g/ml)	1.106	0.998
Temp. of max. density (°C)	11.6	4.0
Viscosity (at 20°C, mPas)	1.25	1.005
Surface tension (at 25°C, µJ)	7.193	7.197
Heat of fusion (cal/mol)	1,515	1,436
Heat of vaporization (cal/mol)	10.864	10.515
pH (at 25°C)	7.41	7.00

Table 1. Physico-chemical properties of heavy water and normal (light) water. Of special interest concerning this text is the about 20% higher viscosity of heavy water.

2.2 Oscillating bulk reaction

The solution of the BZ-reaction was composed from the following ingredients. 1 M sulphuric acid (H₂SO₄), 275 mM malonic acid (C₃H₄O₄), 8.5 mM ammoniumcarnitrate

($\text{CeH}_8\text{N}_8\text{O}_{18}$), 62 mM sodium bromate (BrNaO_3), and 0.4 mM ferroin. The BZ-mixture was given to a beaker and stirred slowly on a magnetic-stirring/heating device at constant rate and controlled temperature ($22\text{ }^\circ\text{C} \pm 0.5\text{ }^\circ\text{C}$). Usually 500ml of the given solution was prepared. Oscillations in these experiments start spontaneously.

3. Waves in thin layers of fluids

The same solution as used in bulk experiments was used in the thin fluid layer experiments. A layer of 2mm height was given into a Petri-dish. Then this dish was treated as described for the gels below. In some experiments higher ferroin concentrations were used, as stated in the experimental section.

3.1 Preparation of gels for the BZ-reaction

The silica gels for the BZ-reaction were made in Petri-dishes (35mm and 100mm diameter) slightly modified according to the procedure described by Yamaguchi et al. (Yamaguchi et al., 1991). A gel-solution containing 9% $\text{Na}_2\text{Si}_2\text{O}_3$, 130 mM H_2SO_4 and 3.3 mM Ferroin was made. In some control experiments, different concentrations of silicate were used (see experimental part), to obtain different viscosities of the gels. A 5mm thick layer of this solution was given into the Petri-dishes. After polymerisation of the gel, the surface of the gels was washed with 330 mM H_2SO_4 two times, and then the gels were covered (5mm high) with a reaction solution containing 330 mM malonic acid, 330 mM NaBrO_3 , and 330 mM H_2SO_4 . The dishes were then immediately mounted in the set-up, it was waited until waves showed up spontaneously and then the video recording was started. The gels were run at room temperature, $20^\circ\text{C} \pm 1^\circ\text{C}$.

3.2 Data evaluation

From all experiments (waves in fluids and gels, and in bulk experiments) video traces were stored on a computer in the avi-format using a standard colour video-camera and a proper frame grabber. The avi-files were changed to stacks of jpg-files by the software VirtualDub^R and imported to the software ImageJ (NIH), alternatively the software LabView^R was used. Using this software, the propagation velocity of the wave-fronts was calculated. Also, from the stacks photos of series of frames were constructed as shown in the figures and single snap-shots were extracted.

4. Experimental results

In a first set of experiments we have investigated the oscillating BZ-reaction (stirred bulk-system without diffusion, convection or buoyancy) in plain light-water and in plain heavy-water. Traces of transmitted blue light through both systems are compared in figure 1. As known from previous studies (Dolzmann et al., 2007) and as can be seen in the figure, upper trace, in normal water there is a short induction period (not shown) followed by a quite stable oscillation (up to hours). At the beginning the peaks of the blue phase are slightly higher, decreasing to a stable value, but then the amplitude as well as period are stable. In the case of heavy water, shown in the lower trace, there is a longer induction period (not shown), followed by some peaks of increasing amplitude. The amplitude stabilizes then for a smaller period, but the period becomes quite big on a short time scale.

Fig. 1. Traces of oscillations of BZ bulk reactions in normal water, upper trace, and in heavy water, lower trace. Significant differences in amplitude and temporal behavior can be seen. The y-axis gives the transmitted light on an arbitrary scaling.

We have shown in a previous study (Dolzmann et al., 2007) that the time course of the single colour changes in the two catalyst system we used has a typical double peak shape at the beginning. In figure 2 it is verified that this behaviour under heavy water is not changed in principal.

Fig. 2. Colour changes of the BZ-bulk reaction on an expanded time scale (compared to figure 1). Left shows the situation in normal water, the right side depicts it in heavy water. The global shape of both recordings is about the same.

Fig. 3. Sequences of frames from waves in fluid BZ-systems. The upper part is from normal water, the lower one from heavy water. Temporal spacing between consecutive frames is 4 seconds; the dishes have a diameter of 100mm. As can be seen, the activity in heavy water is lower over all.

Next we have investigated the behaviour of propagating waves in thin layers of fluids. In principle, in heavy water stable propagating wave fronts were observed, too. The velocity of these fronts was about 3% less compared to the situation in normal water. However, first, the number of excitation centers in heavy water always was lower than in normal water. Second, opposite to normal water, very often the reaction stopped in heavy water after waves had covered the whole dish, but could be reinitiated by shaking the dish and thus starting the reaction again.

To depict the general behaviour, in figure 3 sequences of video frames are shown for both situations.

In addition to the slightly lower propagation velocity in heavy water and the reduced number of excitation centers, very often in the dishes global background colour changes could be observed, see figure 3 background of the frames under heavy water and figure 4, moving much faster than normal waves or possibly being bulk fluctuations.

Assuming the big waves to be propagating bulk-fluctuations, in one and the same system in the presence of heavy water, propagating waves and temporal oscillation would coexist. This was never observed in normal water under comparable conditions.

Finally we investigated propagating waves in gels of BZ medium in normal and in heavy water. Comparable to figure 3 the situation is depicted in figure 5. This time drastic changes in the behaviour of wave propagation could be observed.

Different to the situation in fluid systems, in gels under heavy water the propagation velocity was drastically reduced, 20%, compared to normal water. The waves did not invade the complete gels but died away, creating open fronts and spiral fragments. A more detailed example is shown in figure 6.

Fig. 4. BZ waves in heavy water. As well some normal wave fronts can be seen as also the global colour change in the lower part of the dish.

Fig. 5. Sequences of propagating BZ waves in gels, the upper part shows the situation in normal water, the lower one in heavy water. The temporal spacing between consecutive frames is 4 seconds, the diameter of the dishes is 1100mm. Waves in heavy water are not invading the whole gel and are creating open fronts and spiral fragments obviously.

Fig. 6. Open fronts and spiral fragments in propagating BZ waves in gels made with heavy water.

To learn about the influence of the viscosity of the medium we finally did a series of experiments in gels with increasing concentration of silicate making the gels more stiff and inducing a higher viscosity. The result is shown in figure 7 in a block diagram, the velocity of propagating waves in gels of BZ medium decreases with increasing silicate concentration, meaning with increasing viscosity and thus decreasing diffusion coefficient.

Fig. 7. Velocity of propagating BZ waves in gels made in normal water with increasing amounts of silicate as given in the figure. The propagation velocity decreases with increasing silicate concentration.

5. Discussion

Our experiments in BZ systems oscillating in time demonstrate a reduced excitability, due to the delayed onset of the oscillations. The temporal behaviour results confirm data from previous papers, arguing that the main difference in heavy water in this case is due to

reduced rate constants in the bromation of the organic species (Rossi et al., 2007, 2009). The rate constants in the two catalyst system used describing the interactions between the catalysts are obviously not effected. All this also can be easily verified in doing simulations of the classical reaction schemes using for example the environment MathLab-Simulink, which will be published later.

All the data about the effect of heavy water on oscillating BZ reaction also confirm the statement of it slowing down all biological oscillations and rhythms, although there are by sure totally different basic mechanisms are involved.

Different to oscillating systems in which due to the stirring diffusion, convection and bouyancy do not exist, in case of wave propagation all these phenomena must be taken into account. At least the diffusion of involved species is necessarily included in mathematical models and simulations of wave propagation. On mechanistic reasons one can assume that in case of heavy water, compared to normal water, the diffusion coefficients of all species are reduced, see table in materials and methods. This must be true in addition to the reduced rate constants, see above, which also will be present. Amazingly, in fluid systems the wave propagation velocity was not that much reduced in heavy water, but some other effects pointing out a reduced excitability. In addition, there was the fundamental problem of the coexistence of waves and oscillations in the same system, which has not been described previously.

In gel systems under heavy water conditions, the situation is obviously close to the region in the phase diagram where propagation is no longer possible. First, the velocity was drastically reduced and second, and in the presentation much more obvious, waves are not invading the complete accessible area but die away upon travelling and thereby produce open ended fronts and spiral fragments. Consequently we must assume that the interplay of reduced rate constants and reduced diffusion is inducing the described situation. Our finding that more stiff gels significantly reduce wave propagation velocity but does not induce a brake down of wave fronts seems to verify this statement.

In future investigations, especially in simulations of wave propagation these theories will be tested in detail.

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In the recent decades, there has been a growing interest in micro- and nanotechnology. The advances in nanotechnology give rise to new applications and new types of materials with unique electromagnetic and mechanical properties. This book is devoted to the modern methods in electrodynamics and acoustics, which have been developed to describe wave propagation in these modern materials and nanodevices. The book consists of original works of leading scientists in the field of wave propagation who produced new theoretical and experimental methods in the research field and obtained new and important results. The first part of the book consists of chapters with general mathematical methods and approaches to the problem of wave propagation. A special attention is attracted to the advanced numerical methods fruitfully applied in the field of wave propagation. The second part of the book is devoted to the problems of wave propagation in newly developed metamaterials, micro- and nanostructures and porous media. In this part the interested reader will find important and fundamental results on electromagnetic wave propagation in media with negative refraction index and electromagnetic imaging in devices based on the materials. The third part of the book is devoted to the problems of wave propagation in elastic and piezoelectric media. In the fourth part, the works on the problems of wave propagation in plasma are collected. The fifth, sixth and seventh parts are devoted to the problems of wave propagation in media with chemical reactions, in nonlinear and disperse media, respectively. And finally, in the eighth part of the book some experimental methods in wave propagations are considered. It is necessary to emphasize that this book is not a textbook. It is important that the results combined in it are taken “from the desks of researchers”. Therefore, I am sure that in this book the interested and actively working readers (scientists, engineers and students) will find many interesting results and new ideas.

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