CHEMICAL WAVES AND ACID-BASE DIODES

PhD theses

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2010

INTRODUCTION

The field of nonlinear chemical dynamics has been studied extensively for more than 40 years.[1] This field investigates complex chemical systems far from equilibrium which can be regarded in certain cases as skeleton models of biological systems. Moreover, nonlinear chemical phenomena can produce nano- and microstructures.[2] Two topics of this field, chemical waves and acid-base diodes, are traditional research themes of the Group of Chemical Physics at the Department of Physics.

Waves of excitation (like chemical waves) are usually described using reaction-diffusion equations, but in certain cases a much simpler geometrical approach, the so-called geometrical wave theory, can be also used to describe the propagation of the wave fronts. In this theory, the evolution of a given initial front is determined by the propagation velocity (which is the function of space) using the Fermat's principle of least propagation time.[3] Chemical waves rotating around an obstacle in two dimensional homogeneous media[4] and also in piecewise homogeneous media with circular symmetry[5] were studied previously in our group experimentally and also theoretically using the geometrical wave theory. A numerical method based on the geometrical wave theory was also developed.[6]

An acid-base diode system is another reaction-diffusion system where – in addition – ionic migration also appears. In this electrolyte diode an acidic and an alkaline reservoir are connected and electric voltage is applied between them. The voltage – ionic current characteristic measured in this system resembles to that of a semiconductor diode. In former research the concentration and potential profiles of the diode were investigated analitically,[7] numerically[8] and experimentally.[9] Furthermore, it was found that the current of a reverse-biased diode increased in a nonlinear way if one of the reservoirs was contaminated with salt (positive salt effect).[7]

RESEARCH AIMS

I had the following main aims during my research:

1. To realize experimentally the so-called "chemical lens" being suggested previously using the geometrical wave theory.

2. To study chemical wave propagation theoretically and experimentally in inhomogeneous media with circular symmetry.

3. To model acid-base diodes when both reservoirs are contaminated with salt.

4. To study the ionic conductivity of a new polyvinyl butyral membrane as a connecting element for acid-base diodes, and to compare the properties of this connecting element with those of the PVA gel.

REFERENCES

[1] Epstein, I. R.; Pojman, J. A. *An introduction to nonlinear chemical dynamics*; Oxford University Press: New York, 1998.

[2] Grzybowski, B. A. *Chemistry in motion*; Wiley: Chichester, 2009.

[3] Farkas, H.; Kály-Kullai, K.; Sieniutycz, S. The Fermat Principle and Chemical Waves. In *Variational and Extremum Principles in Macroscopic Systems*; Sieniutycz, S., Farkas, H., szerk.; Elsevier: Oxford, 2005; pp 355–373.

[4] Lázár, A.; Noszticzius, Z.; Farkas, H.; Forsterling, H. Involutes - The geometry of chemical waves rotating in annular membranes. *Chaos* **1995**, *5*, 443–447.

[5] Volford, A.; Simon, P. L.; Farkas, H.; Noszticzius, Z. Rotating chemical waves: theory and experiments. *Phys. A (Amsterdam, Neth.)* **1999**, *274*, 30–49.

[6] Kály-Kullai, K. A fast method to simulate travelling waves in nonhomogeneous chemical or biological media. *J. Math. Chem.* **2003**, *34*, 163–176.

[7] Hegedűs, L.; Kirschner, N.; Wittmann, M.; Simon, P. L.; Noszticzius, Z.; Amemiya, T.; Ohmori, T.; Yamaguchi, T. Nonlinear effects of electrolyte diodes and transistors in a polymer gel medium. *Chaos* **1999**, *9*, 283–297.

[8] Lindner, J.; Snita, D.; Marek, M. Modelling of ionic systems with a narrow acid base boundary. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1348–1354.

[9] Svoboda, M.; Slouka, Z.; Lindner, J.; Snita, D. Direct evidence of concentration and potential profiles in the electrolyte diode. *Chem. Eng. J. (Amsterdam, Neth.)* **2008**, *135*, S203–S209.

1. I realized experimentally a so-called "chemical lens" in two dimensions [T1]. The chemical lense is a piecewise homogeneous medium where the interfacial boundary is a closed aplanatic refracting curve for chemical waves, and the propagation velocity of the waves is smaller inside the aplanatic curve than outside. In this medium perfect image formation is realized: the circular waves initiated at an "object" point in the outer medium travel to a single "image" point in the inner medium after refraction. To create this medium I developed a reactor that consists of a gel containing BZ solution and a membrane with catalyst: the membrane was placed between two gel disks, and certain parts of the membrane were separated from the gels with foils. With this method a piecewise homogeneous medium with a good approximation of the required interfacial boundary was constructed.

2. I studied experimentally and – based on the geometrical wave theory – theoretically chemical waves rotating around an obstacle in continously inhomogeneous media with circular symmetry [T2]. The medium with circular symmetry was realized using the gel + membrane system: concentration gradient between two concentric homogeneous rings ensures the continously changing velocity function. According to the theory, in such a medium two types of front shapes can exist depending on the parameters of the velocity function. I realized both front types in experiments, and compared their shapes with the theoretical ones. In both cases a good agreement was found between theory and experiments. In one case the agreement was extremely good, and in the other case I explained the possible reason for the difference. The front shapes from experiments were also compared with simulations, and a similarly good agreement was found.

3. I worked out new methods to study propagating waves in excitable inhomogeneous media [T2]. I calculated the velocity maps of the media using captured image series of the wave fronts by measuring the local displacement of the points of a front between two subsequent images. Furthermore, the front shapes of an image series were compared with each other in couples and to the difference

of the front shapes their "distance" was assigned. From the distances of an image series a distance matrix was created which is the measure of the change of the front shapes in time.
It can be seen from the velocity maps that the experimental media described in the previous thesis point have no perfect circular symmetry. However, based on the distance matrices stationary front shapes were identified in the experiments and it was found that the shape of the fronts changed nearly periodically.

4. A new micropatterned membrane made of polyvinyl butyral (PVB) was developed for acid-base diodes using the breath figure method. I studied the ionic conductivity of the PVB membrane, and compared it with that of the polyvinyl alcohol (PVA) gel [T3]:
    a) The "diffusion coefficients" of the ions are 4 orders of magnitude smaller in the PVB membrane than those in the PVA gel. At the same time the membrane is thinner by 3 orders of magnitude than the gel, thus altogether the PVB has a faster response to the change of the boundary conditions.

    b) According to the measured characteristics the diffusion coefficients of all ions are nearly equal in the PVB, therefore the Grotthus mechanism that usually occurs in water and in hydro-gels (like PVA gel) does not work in the PVB membrane.

    Furthermore, I studied the current drift which exists in the PVB membrane and in the PVA gel as well.

5. I studied reverse-biased acid-base diodes containing salt in both reservoirs with numerical modelling [T4]. It was observed that a negative salt effect in this case is also possible. Negative salt effect occurs and the current can decrease when salt is added to the acidic reservoir of an acid-base diode whose alkaline reservoir is already contaminated. I studied the negative salt effect in detail and deduced a semiquantitative explanation. Using this effect the diode current can have sensitive response to small ion concentrations. The negative salt effect has also been proved experimentally.

PUBLICATIONS RELATED TO THE NEW SCIENTIFIC RESULTS

[T1] Kály-Kullai, K.; Roszol, L.; Volford, A. Chemical lens. *Chem. Phys. Lett.* **2005**, *414*, 326–330.

[T2] Roszol, L.; Kály-Kullai, K.; Volford, A. Chemical waves in inhomogeneous media with circular symmetry. *Chem. Phys. Lett.* **2009**, *478*, 75–79.

[T3] Roszol, L.; Lawson, T.; Koncz, V.; Noszticzius, Z.; Wittmann, M.; Sarkadi, T.; Koppa, P. A micropatterned polyvinyl butyral membrane for acid-base diodes. *J. Phys. Chem. B* **2010**, (accepted).

[T4] Roszol, L.; Várnai, A.; Lorántfy, B.; Noszticzius, Z.; Wittmann, M. Negative salt effect in an acid-base diode: Simulations and experiments. *J. Chem. Phys.* **2010**, *132*, 064902.

OTHER PUBLICATIONS

[T5] Szakály, T.; Lagzi, I.; Izsák, F.; Roszol, L.; Volford, A. Stochastic cellular automata modeling of excitable systems. *Cent. Eur. J. Phys.* **2007**, *5*, 471–486.