PATTERN FORMATION IN THE METHYLENE BLUE–FRUCTOSE–OXYGEN SYSTEM IN AQUEOUS SOLUTION AND IN GEL SYSTEMS

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Dedicated to Professor Ľudovít Treindl on the occasion of his 70th birthday in recognition of his outstanding contributions to chemical kinetics and oscillating reactions.

Spatial patterns in methylene blue-catalyzed oxidation of fructose at alkaline pH were found in aqueous solution and in gel systems. In a thin liquid layer (thickness >2.4 mm) a mixture of spots and stripes was formed by interaction of a nonlinear reaction and the Rayleigh or Maragoni instabilities. The pattern formation was affected by initial reactant concentrations and by the thickness of the reaction mixture layer. Long-lasting structures were formed in gel systems (polyacrylamide, agar, gelatin). These patterns also arise primarily from hydrodynamic processes.
Key words: Pattern formation; Gels; Interfaces; Methylene blue; Fructose; Oxygen; Oxidations; Oscillating reactions.

Dissipative structures in systems kept far from equilibrium result from a symmetry-breaking instability of the basic thermodynamic state induced by nonlinearities and competition between antagonistic processes[1]. Pattern formation in hydrodynamic systems can be the result of an unstable density gradient. Such an unstable density gradient can be caused, *e.g.*, by temperature[2], chemical concentrations[3] or by surface tension effects[4]. The convective patterns arising *via* the Rayleigh or Marangoni instabilities strongly resemble the Turing structures. Spatial structures due to instabilities in reaction–diffusion systems, so-called Turing structures, have been for some time and still are of interest[5–7]. The Turing structures were observed experimentally for the first time in a chemical system, the CIMA (ClO_2^-/I^-/malonic acid) reaction, in a continuously fed gel reactor[1,6,7].

The other oscillatory chemical system, reported to be capable of forming the Turing-like structures in a gel matrix[8,9], is the methylene blue oscillator[10] which consists of methylene blue, sulfide and oxygen (PA–MBO). In

this system, a variety of spatial structures such as hexagons, stripes and zig-zag patterns have been found. Recently Orban *et al.*[11] reported the formation of similar patterns during the polymerization of acrylamide in the presence of sulfide ions. They concluded that methylene blue is not an essential species for the formation of patterns and that the patterns arise from the Rayleigh–Bénard or Marangoni instabilities.

In the PA–MBO reaction, complex chevron and honeycomb patterns have been recently reported by Steinbock, Kasper and Müller[12]. The presented results emphasised that the pattern formation in this system cannot be explained on the basis of hydrodynamic considerations alone, since the observed transitions to patterns of higher complexity occur after gelation and after formation of hexagons. The fundamental questions whether the initial hexagonal patterns arise primarily from hydrodynamic or reaction–diffusion processes remain unanswered. Yatsimirskii *et al.*[13] found that different self-organization phenomena occur during different substrate oxidations by air dioxygen. We have found that the pattern formation can be observed when a solution containing NaOH, monosaccharide and dye (the so-called "Blue Bottle" experiment) is poured into an open Petri dish[14,15].

In this work, we present spatial pattern formation found in a system containing methylene blue, fructose, NaOH and molecular oxygen (MBFO) in aqueous solutions and in gel systems (polyacrylamide, agar, gelatin).

EXPERIMENTAL

All chemicals were of analytical grade (Merck) and were used without further purification. The solutions were freshly prepared with doubly ion-exchanged water. Observations of patterns were performed under semibatch conditions in the Petri dish which allows exchange of oxygen between the solution and the surrounding atmosphere. Thus the system is open with respect to molecular oxygen but closed with respect to the other species.

The polyacrylamide gel was prepared from the following aqueous stock solutions[8,16]: acrylamide (AA) (20 g per 100 ml), *N,N*'-methylenebisacrylamide (BIS) (0.5 g per 25 ml), triethanolamine (TEA) (3 g per 10 ml) and ammonium peroxodisulfate (2 g per 10 ml). A typical procedure of mixing the gel components with the MBFO solutions is as follows: First, 0.48 ml BIS and 0.5 ml TEA solution were added to 6.33 ml of AA solution. Then a mixture of calculated amounts of methylene blue and fructose was added. Before starting the polymerization with 0.25 ml of ammonium peroxodisulfate, double-distilled water was added to reach a final volume of 15 ml. The whole mixture was poured into the Petri dish *ca* 90 mm in diameter. The depth of the reaction mixture, calculated from the reaction mixture volume and area of the Petri dish, was 2.4 mm.

The agar gel layer was prepared by boiling, the stock solution of agar (1 g of agar in 100 ml of distilled water) for a few minutes and stirring the hot solution intensively with an ultrasonic compact cleaner for about 30 min. The solution was filtered and the amount of missing water was added. Then, 0.72 ml of 2 M NaOH, 0.24 ml of 0.5 M fructose and 0.0034 g of

methylene blue were added to 14.4 ml of agar solution (at *ca* 50 °C) and the mixture was poured into the Petri dish.

The gelatin layer was prepared by adding 7.5 g of gelatin to 50 ml of distilled water at 70 °C and heating and stirring the solution continuously until 90 °C was reached. Then, 1 ml of 0.5 M fructose, 1 ml of 0.01 M methylene blue and 3 ml of 2 M NaOH were added to 15 ml of the filtered solution. After a thorough mixing, the solution was poured into the Petri dish.

The experiments were done in the daylight, mostly at room temperature.

RESULTS AND DISCUSSION

In the nonlinear chemical system used for our study, the overall chemical reaction is the methylene blue-catalyzed oxidation of monosaccharide with O_2 in an unbuffered alkaline solution. Methylene blue exists in two stable forms, MB^+ and MBH. The oxidized form (MB^+) is blue, while the reduced form (MBH) is colourless. The redox relation between these two forms includes a radical intermediate ($MB^\bullet$):

$$MB^+ + e \; \rightleftharpoons \; MB^\bullet \tag{1}$$

$$MB^\bullet + e + H^+ \; \rightleftharpoons \; MBH \tag{2}$$

A kinetic study of oxidation of D-glucose with methylene blue in the presence or in the absence of oxygen as a component reaction of the Blue Bottle experiment was reported[17].

The Methylene Blue–Fructose–O_2 System (MBFO) in Water Solutions

A thoroughly mixed solution containing 0.5 M NaOH, 0.008 M fructose and $2 \cdot 10^{-4}$ M MB^+ was poured into the Petri dish making a layer of 2.4 mm or more. After a few minutes, the onset of colourless structures in the otherwise blue solution became visible in the undisturbed and uncovered solution (Fig. 1). The induction period (IP) is defined as the time between the pouring the solution into the Petri dish and the beginning of the pattern formation. In the course of the reaction a very slowly changing but as a whole stable mosaic pattern developed and persisted approximately for 2–3 h. The patterns are transient because the system evolves towards thermodynamic equilibrium.

   Stirring the liquid in the Petri dish produced a homogeneous blue colouration. Upon standing, the blue liquid reverts to its original pattern within a few minutes. This process can be repeated many times. No regular patterns were observed with solution layers of 2.2 mm thickness or less.

   The effect of oxygen was assessed by comparing experiments run in air and in nitrogen atmosphere. In the presence of N_2, no pattern formation was seen in the reaction mixture. This indicates that O_2, which affects the chemical reaction and/or evaporation, plays a fundamental role in the pattern formation. If the Petri dish was filled with solution up to the rim, and then covered with a glass plate, *i.e.*, the liquid–air interface was replaced by a liquid–glass interface, the structure was not obtained. When an air gap between the liquid surface and the glass seal was left in a sealed Petri dish, the structures developed in the usual way. Neither the addition of 25 vol.% methanol in order to enhance the evaporation patterns, nor the addition of surfactants appeared to affect the pattern evolution.

   The pattern formation could be seen over a wide range of fructose concentrations ($0.006–0.05$ mol l^{-1}) and NaOH concentrations ($0.4–1.0$ mol l^{-1}). The induction period decreased with increasing concentration of fructose and NaOH. The temperature ranged from 20 to 40 °C and the length of IP decreased with temperature. For 20 and 40 °C, the induction periods were 130 and 48 s. The patterns were also sensitive to temperature. This is associated with the fact that the solubility of O_2 decreases as the solution temperature increases. The pattern formation was relatively little affected by the thickness of the reaction mixture layer; the average wavelength of the patterns and IP increased with the depth of the liquid. The surface area of the solution (38.5, 63.6 and 147.3 cm^2) did not have any noticeable effect on the pattern formation. The IP increased with increasing surface area.

   Some of our observations suggest that chemical reaction at the liquid–liquid or liquid–gas interfaces is necessary for the structure evolution. Avnir

Fig. 1
Pattern formation in the MBFO aqueous system. The dark colour corresponds to the oxidized form and the white regions to the reduced form of methylene blue. Initial reactant concentrations (mol l^{-1}): $[NaOH]_0$ 0.5, $[MB^+]_0$ $2.0 \cdot 10^{-4}$, $[F]_0$ $8.0 \cdot 10^{-3}$; $T = 20$ °C. The Petri dish 9 cm in diameter was filled to a height of 2.4 mm. The picture was taken 5 min after the start of the experiment
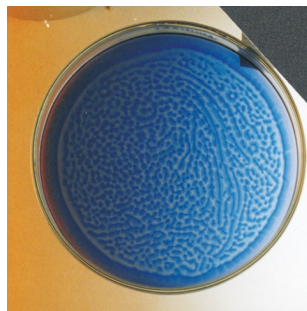
and Kagan[18] showed that the reaction between a diffusing gas and a reactant in solution proceeds in a nonhomogeneous structured way. The MBFO reaction consumes oxygen from air and the reaction therefore starts at the surface of the liquid. This results in concentration and surface-tension gradients in the plane of the liquid surface. *Via* hydrodynamic rolls induced by the Bénard–Marangoni convection, oxygen is transported into deeper layers in the solution. If the surface was covered with a layer of hexane (2, 3 or 4 mm), the set of blue halfwaves was formed which broke into a typical series of dots after some time. Oxygen is soluble in hexane and can diffuse into the system. In the regions of high O_2 concentration, MBH can be oxidized to MB^+, and thus the blue-coloured mosaic patterns appear. The oxidation is possible only in regions with relatively high O_2 concentrations, because MB^+ is reduced with fructose to MBH at low O_2 concentrations. The presence of fructose, O_2 and methylene blue in the initial mixture are essential for the development of patterns in aqueous solutions.

The reduction of MB^+ with fructose in the presence or absence of O_2 are the most complex parts of the reaction mechanism. Figure 2 shows simultaneous spectrophotometric measurement of $[MB^+]$ and amperometric measurement of $[O_2]$ during oxidation of fructose with MB^+ in the presence of O_2 (curves *1* and *2*, respectively). The reaction passes through two stages. In the first stage, the net reduction of MB^+ proceeds to a very small extent (see
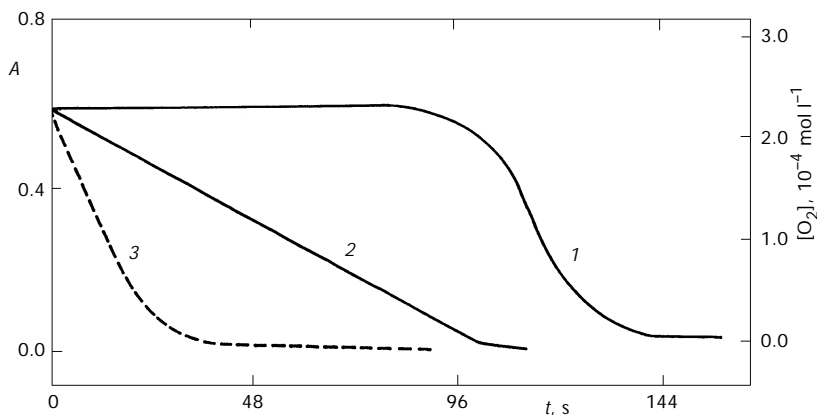

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Kinetics of the reaction of MB^+ with fructose. *1* Absorbance, *A*, at the isosbestic point at 600 nm of MB in the alkaline solution; *2* the response of an O_2 electrode in the presence of the dissolved O_2; *3* the absorbance, *A*, due to MB^+ at 600 nm in the absence of O_2. Initial concentrations of individual components (mol l^{-1}): $[NaOH]_0$ 0.05, $[MB^+]_0$ $5 \cdot 10^{-5}$, $[F]_0$ 0.1, $[O_2]_0$ $2.4 \cdot 10^{-4}$; T = 20 °C

a plateau on curve *1*), but O_2 is rapidly removed in a zeroth-order process (see curve *2*). In the second stage, concentration of O_2 is too low to be measured and the reduction of MB^+ occurs quite rapidly. These results demonstrate that fructose is easily oxidized with MB^+ and if molecular oxygen is present, the leucomethylene blue (MBH) produced is much more rapidly reoxidized to MB^+. Curve *3* describes the reaction in the absence of O_2. In this case, the MB^+ concentration decreased exponentially in the course of the reaction.

Very recently, Pons *et al.*[19] studied pattern formation in the methylene blue–glucose system in aqueous solutions. We can conclude that our results described above are in accordance with the results of Pons *et al.*[19].

The Methylene Blue–Fructose–O_2 System in the Polyacrylamide Gel (PA–MBFO)

The influence of the hydrodynamic convection on the pattern formation is suppressed in gel systems. Theoretical results obtained for the reaction–diffusion systems, such as Turing structures[5], are comparable only with results of the experiments where the hydrodynamic effect is thoroughly eliminated. The gel components, acrylamide, *N,N'*-methylenebisacrylamide, triethanolamine and water were mixed and then ammonium peroxodisulfate $(NH_4)_2S_2O_8$ was added to initiate the gelation process. Molecular oxygen from air was also present. (The concentrations are given in the caption to Fig. 3 and are the same as in ref.[8].) The final volume was 15 ml, which formed *ca* 2.4 mm solution layer. The labyrinthial pattern appeared in the pure polyacrylamide gel about 30 min after the mixture was poured into the Petri dish (Fig. 3). The surface of the gel pattern was initially smooth but later on, the changes due to inhomogeneous swelling and/or shrinking of the gel could be observed. Initial addition of NaOH to the gel results in finer pattern formation.

FIG. 3
Pattern formation in the pure polyacrylamide gel; the same conditions as in Fig. 1 in the AA–BIS–TEA–$S_2O_8^{2-}$ system. The concentrations are given in the Experimental

In the PA–MBFO system, the gel components were mixed with methylene blue, fructose and molecular oxygen from air. The first type of pattern arose approximately 5–10 min after the beginning of experiment and was composed of white circles, deformed spots, or stripes, depending on the composition of the system. The presence of NaOH in the initial mixture is not essential for the development of pattern because pH of the polyacrylamide gel is about 9. However, in some experiments, NaOH was added to increse the pH of the system. The presence of all components (MB^+, F, O_2) in the initial mixture is essential for the development of patterns of the first type.

The patterns formation observed in the PA–MBFO system is a result of a combination of chemical and physical processes occurring during polymerization. The polymerization of acrylamide is highly exothermic[11]. The patterns are affected by the thickness of the reaction mixture layer. The distance between dots increases with the increasing solution layer thickness. The observed distances between dots (or lines) were approximately 1 and 3 mm for 2.4 and 4.8 mm solution depths. If the surface was covered with a layer of hexane (3 mm), the pattern appeared. The surface area of the gel did not have any noticeable effect on the pattern formation. The first type of pattern persisted for several hours. During this time, the gel underwent only a slight swelling and the structure evolved in time. The second type of pattern was formed about 20 h after mixing all the components of the PA–MBFO system (Fig. 4). These structures were completely stationary and resemble the swollen bubble pattern[20].

We assume that the first pattern arises from the Rayleigh–Bénard and/or Bénard–Marangoni instabilities as in aqueous solutions. The second pattern indicates an interaction between the polyacrylamide gel and the MBFO reaction components. They are associated with mechanical and/or chemical changes in the polyacrylamide network. In the CIMA reaction, Lee *et al.*[21] observed a similar swelling phenomenon.
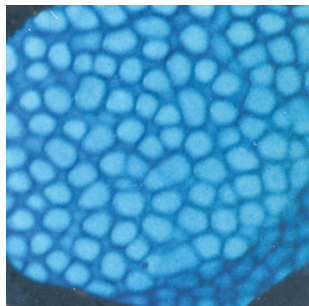

Fig. 4
Stationary patterns in the PA–MBFO system 20 h after mixing. The same composition of the gel mixture as in Fig. 3 plus $6 \cdot 10^{-4}$ M MB^+ and $8 \cdot 10^{-3}$ M F. The layer thickness 2.4 mm

MBFO in Agar and in Gelatin

The patterns could be also found in experiments with other gels such as agar or gelatin. In the agar–MBFO reaction, patterns arise *ca* 2–4 min after preparation (Fig. 5). The time required for solidification of the mixture is about 17 min. The patterns remain visible for about 1 h; they are, however, transient in nature since the system evolves towards thermodynamic equilibrium. The wavelength of the pattern increases as the gel thickness increases. After 10 h, the fossilized pattern can be seen in the agar gel layer. The structures seen in the agar–MBFO system arise from a chemically driven convective instability.

The convective patterns arise also in the gelatine–MBFO system (Fig. 6). Our experiments show that in agar and gelatin media, the behaviour of the reaction system is closer to plain aqueous solution than in the polyacrylamide medium.
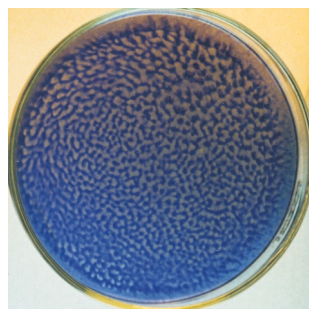

Fig. 5
Pattern formation in the agar–MBFO system. Initial reactant concentrations (mol l^{-1}): $[NaOH]_0$ 0.1, $]MB^+]_0$ $6 \cdot 10^{-4}$, $[F]_0$ $8 \cdot 10^{-3}$ in 1% agar. The layer thickness 2.4 mm
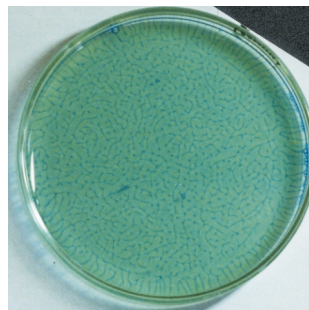

Fig. 6
Pattern formation in the gelatin–MBFO system. Initial reactant concentrations (mol l^{-1}): $[NaOH]_0$ 0.3, $[MB^+]_0$ $5 \cdot 10^{-4}$, $[F]_0$ $2.5 \cdot 10^{-2}$ in 15% gelatin. The layer thickness 3.1 mm. Picture was taken 8 min after mixing the components and layering the solution into the Petri dish

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