SPATIAL STRUCTURES IN AN UNCATALYZED BROMATE OSCILLATOR AND PERIODIC PRECIPITATION IN GELS

Lubica ADAMCIKOVA, Vladislav HOLBA and Viera PARKANIOVA

Department of Physical Chemistry,
Comenius University, 842 15 Bratislava, The Slovak Republic

Stationary and moving structures in the uncatalyzed bromate–aniline–sulfuric acid oscillator and the formation of Liesegang rings in gelatin and silica gel were investigated. Structural analogies were found in the systems which are of a different nature. They exhibit properties typical of Turing type structures.

The Belousov–Zhabotinskii (BZ) reaction of bromination of malonic acid by bromate ions in the presence of a ferrous phenanthroline (ferroin) catalyst is a striking example of spatiotemporal pattern formation in chemical systems[1]. Concentric blue rings, known as target patterns, can develop spontaneously in the initially homogeneous red solution and propagate outwards from their centers. If the rings are sheared, mechanically or due to concentration gradients, they transform into propagating spirals. Stationary and moving structures have been observed by Orbán[2] in uncatalyzed bromate oscillators. In addition to a trigger wave behavior similar to that exhibited by the BZ reaction, the uncatalyzed reactions can also give rise to a patterned precipitate which undergoes cyclic dissolution and precipitation.

Many experiments investigating spatial pattern formation in chemical reactions conducted in gel systems[3–8] have been carried out in the past years. This growing interest in work with gels has been motivated by their explicit advantages over aqueous systems. The influence of hydrodynamic convection on wave propagation is suppressed in gel systems. Theoretical results obtained for reaction-diffusion systems, such as Turing structures[9], are only comparable with the results of experiments where the hydrodynamic effect is thoroughly eliminated. In 1990, Castets et al.[10] reported on the first unambiguous experimental evidence of the existence of symmetry breaking reaction-diffusion structures in a gel reaction as predicted by Turing.

A periodic precipitation process in gelation known as the Liesegang ring formation[11] has been investigated over the past 90 years. If an electrolyte forms a sparingly soluble salt with another electrolyte which is dissolved in a gel, the precipitation does not proceed continuously; instead, concentric rings, spirals and other periodic structures of

the precipitate are formed[12]. Various theories have been put forward to account for the Liesegang phenomenon. Recent development has led to the formulation of reaction-diffusion and reaction-diffusion-nucleation equations for periodic precipitation processes[13,14].

This paper is concerned with spatial structures appearing in the aniline–bromate–H_2SO_4 system containing gelatin or silica hydrogel and with periodic silver dichromate precipitation in the two gels. Some remarkable similarities between the systems were observed.

EXPERIMENTAL

Solutions were prepared with doubly distilled water and reagent grade chemicals. The experiments consisting in mixing the reagents and pouring the mixture into a Petri dish (usually 95 mm in diameter) were performed at 23 ± 0.5 °C. A sodium silicate solution (Merck) which contained 25.5 – 28.5% SiO_2 was employed. Stock solutions containing 2.7, 3.4 4.05, 6.1, and 8.1 wt.% sodium silicate were prepared by dissolving appropriate volumes of the sodium silicate in doubly distilled water. The solutions were boiled for several minutes and kept hot while stirring vigorously by means of an ultrasonic compact cleaner for about 30 min. After cooling down to room temperature, the solutions were filtered, and the evaporated water was replenished[8]. Solutions of 10, 15, 20, 25, and 30 wt.% of Gelatine Animalis CSL 3, Medika TESON 1 Bratislava in doubly distilled water were used for experiments with Liesegang rings. The gelatin layer was prepared as described in ref.[15]. Sodium silicate gels employed in the periodic precipitation were as in the BZ experiments. The concentration of potassium dichromate in SiO_2 lay within the range of 0.001 – 0.01 mol l^{-1}. The spatial arrangement of Liesegang rings was measured by means of a travelling microscope (Abbe Komparator, Zeiss Jena), and the periodic structures were recorded with a microdensitometric assembly described in ref.[16]. The viscosities were measured with an Ostwald viscometer at 25 °C.

RESULTS AND DISCUSSION

Uncatalyzed Oscillatory Chemical Reaction

Three types of spatial structures were observed in thin unstirred layers in the aniline–acid–bromate systems in silica hydrogel and gelatin, as in water[2]. Stationary mosaic structures, trigger waves, and transient stripe structures appeared in dependence on the reactant mixing mode.

Uncatalyzed Oscillatory-Stationary Mosaic Structures

Such structures appeared if the appropriate amounts of aniline and sodium bromate were added to a gel solution which had been prepared by dissolving the gel (gelatin or silica gel) in H_2SO_4. The solution was thoroughly mixed and added uniformly to a Petri dish. Mosaic structures with sharp boundaries arose several minutes after the beginning of experiment (Fig. 1). The development of the mosaic pattern was accompanied by the

formation of a precipitate. The insoluble substance precipitated from the dark bands in the patterns and remained on the bottom of the Petri dish as long as several months. The pattern formation was affected by the thickness of the reaction mixture layer, which was calculated from the reaction mixture volume and Petri dish area. The calculated thickness values are approximate only because no correction was made for the solution adhering to the Petri dish walls by capillary forces. The size of the "small-cell structure" was measured as the cell width by means of an Abbé Komparator and also determined by counting clear spots (cells) per unit area (Table I). The size of the cells increased with increasing solution layer thickness while the cell count per cm^2 decreased. The size of the cells was independent of the concentrations of the gels, bromate ions and aniline, as well as of the Petri dish diameter at a constant solution layer thickness. Stationary mosaic structures were observed at $NaBrO_3$ concentrations of 0.02 to 0.4 mol l^{-1} in a gel solution containing 2.2 mol l^{-1} H_2SO_4 and 0.022 mol l^{-1} aniline,

TABLE I
Size and number of cells in layers of a system composed of 15% gelatin, 2.2 mol l^{-1} H_2SO_4, 0.022 mol l^{-1} aniline, and 0.055 mol l^{-1} $NaBrO_3$

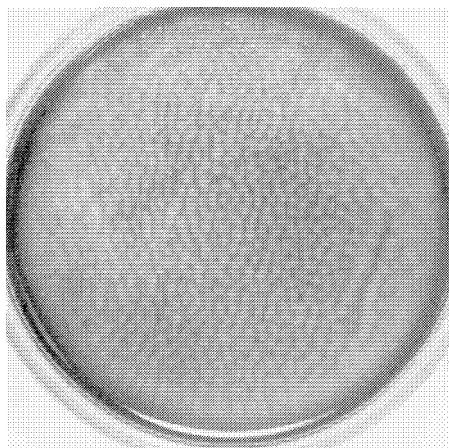| Solution layer thickness mm	Average cell width mm	Cell count per cm^2
0.7	1.04	34
1.0	1.53	26
1.26	2.02	20
1.5	3.11	8
2.0	4.01	5

FIG. 1
The mosaic pattern in the aniline–acid bromate system in 15% gelatin. Initial reactant concentrations (mol l^{-1}): H_2SO_4 2.2, aniline 0.022, $NaBrO_3$ 0.055. Layer thickness 1.5 mm

and at aniline concentrations of 0.001 to 0.25 mol l^{-1} in a gel solution containing 2.2 mol l^{-1} H$_2$SO$_4$ and 0.055 mol l^{-1} NaBrO$_3$. The arrangement of the cells with mosaic structures was different at different concentrations of bromate. At higher initial bromate concentrations, the cells were connected to parallel bands, whereas at lower bromate concentration, they were connected to rings. Experiments were carried out to investigate possible surface effects involved in the pattern formation. The surface-active cation–tetrabutylammonium iodide – and the surface-active anion – sodium dodecyl sulfate – were added to the reaction mixture. At initial concentrations of surfactants 1 and 5 mmol l^{-1}, the mosaic structures appeared and developed in a manner similar to experiments where the surfactants were absent. Later, roughly in 180 min, the formation of bands was observed.

If the Petri dish was protected from air with a glass cover, no mosaic structures appeared in the reaction mixture. This indicates that surface effects play a fundamental role in the mosaic formation. Such effects may include volatilization of a reaction component (such as Br$_2$) or dissolution of a component in air which affects the chemical reaction or a possible surface tension – surface concentration convective instability. Under our experimental conditions Br$_2$ is evolved and autocatalytic generation of HBrO$_2$ is known to be controlled by HOBr as it is by bromide. The bromate–aniline colloidal suspension may also play a role in the instability. The mosaic structure seems to be composed of a set of convective cells created in the layer due to instability of the liquid/gas interface of the suspension.

In addition to the systems where the patterns can be basically modelled by a reaction-diffusion mechanism, new types of spatial organization are generated by the effect of convective flow and interfacial instability, as observed in this system in dilute gels (Fig. 2).
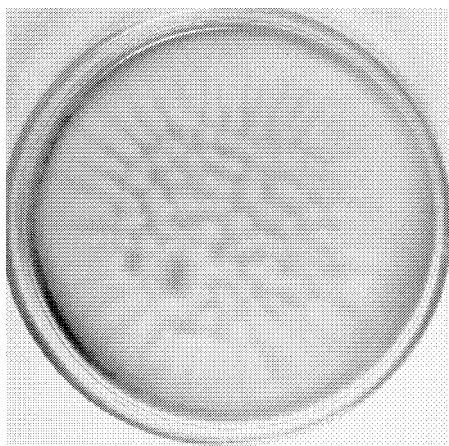

Fig. 2
Stationary chemical irregular structure in 1.35% silica gel. Layer thickness 1.25 mm, initial concentrations as in Fig. 1

Uncatalyzed Oscillatory Trigger Waves with a "kiwi" Structure

The solutions were prepared in 15% gelatin or in 2.02% silica gel. Predetermined volumes of sulfuric acid, aniline and water were mixed and added slowly to the stirred gelatin or waterglass solution, and the mixture was poured into a Petri dish to gelate. In sixty minutes, the reaction was triggered by adding a drop of the appropriate amount of bromate to the center of the gel layer. Chemical circle waves propagated from this center as rings, called trigger waves. Initially, the solution was homogeneous. The waves propagated at a velocity of several millimeters per minute. In addition to the circle waves, the stripes which connected two adjacent circle waves were also observed. (Since this structure looked like a fruit of kiwi, transverse cut up, we called it a "kiwi" structure.)

The kinetics of the BZ reaction in gels is reflected by the velocity of the trigger waves, v, which is mainly determined by the autocatalytic reaction step coupled with diffusion[18,19],

$$v = (4kD\,[\mathrm{H^+}][\mathrm{BrO_3^-}])^{1/2} \ , \tag{1}$$

where k is the rate constant of this step and D is the diffusion coefficient of $\mathrm{HBrO_2}$. We measured the velocity of the first appearing circular wave in the two gels at different initial bromate concentrations. A linear dependence of v (mm min^{-1}) on $[\mathrm{H^+}]^{1/2}$ $[\mathrm{BrO_3^-}]^{1/2}$ (mol l^{-1}) was found,

$$v = a + b\,[\mathrm{H^+}]^{1/2}\,[\mathrm{BrO_3^-}]^{1/2} \ , \tag{2}$$

where $a = -3.87$, $b = 24.9$ for gelatin, and $a = -1.33$, $b = 22.9$ for silica gel. Based on the slopes of the dependences, which provide $(4kD)^{1/2}$ in Eq. (*1*), the rate constants of $k = 28.47$ mol^{-2} l^2 s^{-1} in 15% gelatin and $k = 24.4$ mol^{-2} l^2 s^{-1} in 1.7% silica gel were obtained using $1.5 \cdot 10^{-5}$ cm^2 s^{-1} for the diffusion coefficient for $\mathrm{HBrO_2}$. So, we were able to determine the rate constant of an important autocatalytic reaction in the BZ reaction, viz.

$$\mathrm{d[HBrO_2]}/\mathrm{d}t = k\,[\mathrm{H^+}]\,[\mathrm{BrO_3^-}]\,[\mathrm{HBrO_2}] \ , \tag{3}$$

in the two gels. The rate constant of this reaction in water is $k = 20$ mol^{-2} l^2 s^{-1} (refs[17–19]).

According to Eq. (*1*), the velocity of propagation should be proportional to $D^{1/2}$. The diffusion coefficients were changed by modifying viscosity of the solution. Gelatin and

silica gels were added in various concentrations to increase the viscosity without affecting the kinetics. The viscosity was measured, and the product of viscosity η and the diffusion coefficient D was assumed to be constant to a reasonable approximation (Walden's rule).

The plot of the average velocity of propagation vs $\eta^{1/2}$ is linear, which indicates that the velocity of propagation is proportional to the square root of the diffusion coefficient, in agreement with theoretical and experimental models[20,21]. Our experimental studies suggest that the trigger wave propagation is a result of a coupling of the autocatalytic mechanism and diffusion. No significant difference in the velocities of propagation exists between the uncovered and covered solutions.

Uncatalyzed Oscillatory-Trigger Waves in Solid Silica Gels

The method of preparation was as before but the reaction was triggered by injecting a drop of bromate only after the gel became solid (roughly in 6 h). Chemical circular waves appeared in this reaction mixture as blue and brown rings, which evolved for 20 h like Liesegang rings. An example of a fully developed stationary concentration structure is shown in Fig. 3.

Uncatalyzed Oscillatory-Transient Stripe Structures

Aniline and aqueous sodium silicate or gelatin were mixed, and the solution was poured into a Petri dish. Subsequently, this gel system was brought in contact with a mixture containing $NaBrO_3$ and sulfuric acid. The stripe structure appeared in a few seconds and persisted approximately for 20 min.
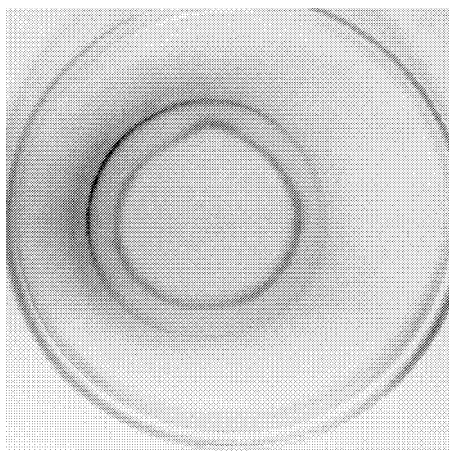

FIG. 3
Trigger waves in solid silica gel 4 h after starting the reaction by adding $NaBrO_3$ to the center of the Petri dish. Concentrations in 1.7% silica gel (mol l^{-1}): H_2SO_4 2.2, aniline 0.022, $NaBrO_3$ 0.055

Liesegang Rings

The results of microscopic and microdensitometric measurements of the positions of the Liesegang rings can be summarized into a simple spacing law, which in the experimental conditions applied has the form[22]

$$x_N = x_0 \, p^N \, , \tag{4}$$

where x_N is the ring location, N is the ring number, and x_0 and p are constants. Equation (*4*) was only satisfied for $N = 1$ to 6 in gelatin, and for $N = 1$ to 9 in silica gel, for which the spacing laws were $x_N = x_0 \, (1.2325 \pm 0.0041)^N$, and $x_N = x_0 \, (1.0012 \pm 0.0066)^N$, respectively. The experiments indicate that the formation of precipitation patterns in the two gels investigated obeys the same laws. The development of Liesegang rings near the border of the gelatin layer displays an interesting effect, viz. breaking of the structure: The formation of concentric rings ceases and a system of strips appears (Fig. 4). In a similar experiment using gel, however, the rings transformed into a mosaic structure.

Comparison of the Uncatalyzed BZ Reaction in Solid Silica Gel and Liesegang Rings

Structural analogies were found although the nature of the systems is apparently different. They exhibit properties typical of Turing type structures.

They are stationary concentration patterns originating from the coupling of reaction and diffusion processes. The development of the patterns is accompanied by separation of a precipitate. Their kinetics include autocatalysis. The BrO_3^-–aniline–H_2SO_4 system
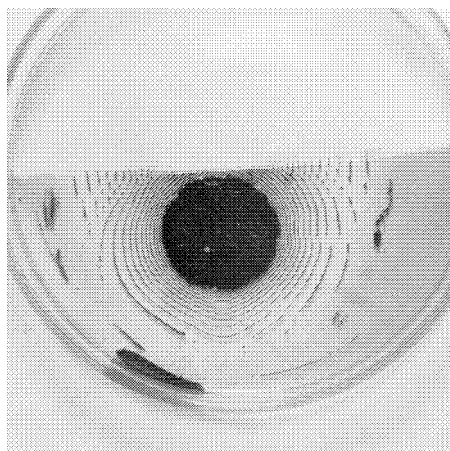

FIG. 4

The breaking of Liesegang rings near the gelatin layer border. Composition: 15% gelatin, 0.01 mol l^{-1} $K_2Cr_2O_7$, concentrated $AgNO_3$ solution

exhibits oscillatory behavior, while, on the other hand, the autocatalytic nature of colloidal particle growth has been shown to be an important step in the Liesegang phenomenon[23]. Aniline and $Cr_2O_7^{2-}$ diffuse more slowly than bromate and Ag^+, the difference being due to diffusion processes in the gel. Aniline and $Cr_2O_7^{2-}$ were fixed in a thin solid layer of SiO_2. The patterns have an intrinsic wavelength which is independent of the geometrical parameters of the system. The formation of symmetry breaking patterns was also observed.

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