Temperature control of pattern formation in the $\text{Ru}(\text{bpy})_3^{2+}$ -catalyzed BZ-AOT system

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Received 26th August 2008, Accepted 20th November 2008

First published as an Advance Article on the web 19th January 2009

DOI: 10.1039/b814825b

Using temperature as a control parameter, we observe a transition from stationary Turing patterns at $T = 15\text{--}20\text{ }^\circ\text{C}$ to traveling waves at $T = 50\text{ }^\circ\text{C}$ (and above) in the $\text{Ru}(\text{bpy})_3^{2+}$ -catalyzed Belousov–Zhabotinsky (BZ) reaction incorporated into the water nanodroplets of a water-in-oil aerosol OT (AOT) microemulsion. At constant chemical composition, molar ratio and droplet fraction, the transition takes place *via* a series of stable patterns, including oscillatory Turing patterns (at $35\text{--}40\text{ }^\circ\text{C}$) and reversed oscillatory Turing patterns (at $50\text{ }^\circ\text{C}$). We attribute the pattern transitions to a temperature-induced percolation transition of the BZ-AOT microemulsion, implying a change from isolated water nanodroplets to a system-spanning network of water channels.

1. Introduction

Developing the ability to control pattern formation in reaction–diffusion systems has been an active area of research for a number of years.¹ Such control can offer important practical applications^{2–4} in addition to extending our understanding of the mechanism of pattern formation. Amongst chemical systems that can sustain pattern formation, the Belousov–Zhabotinsky (BZ) reaction introduced into a microemulsion with the surfactant sodium bis(2-ethylhexyl)sulfosuccinate (aerosol OT = AOT) (BZ-AOT system⁵) is especially attractive due to the rich variety of patterns it can display. Examples include Turing patterns,⁶ standing and packet waves,⁷ anti-spirals,⁸ oscillons,⁹ dash waves¹⁰ and segmented spirals.^{10,11} The wealth of behaviour found in this system as the composition is varied raises questions regarding the ability to control transitions between different patterns in a microemulsion of fixed composition by changing an external parameter.

The most common method used to control dissipative patterns is illumination of the system.^{12–16} Temperature has also been used as a control parameter.¹⁷ In the BZ-AOT system, temperature can affect patterns not only by changing reaction rates, but also by changing the structural properties of the microemulsion due to induction of the percolation transition.^{18–21} Below the percolation point, the microemulsion can be considered to exist as well-defined water nanodroplets isolated in the oil phase. Above the percolation transition, the microemulsion consists of aggregates of water molecules (or clusters of water nanodroplets) that form system-spanning networks. The diffusion coefficients of water-soluble species, which strongly influence patterns in the BZ-AOT system, are very different above and below the percolation point.²²

The percolation transition point, and the structure of an AOT microemulsion, depend on two important parameters: the molar ratio ω ($= [\text{H}_2\text{O}]/[\text{AOT}]$) and the droplet fraction ϕ_d ($=$ total volume fraction of water and AOT molecules). The ratio ω approximately determines the mean radius R_w of the water droplets as $R_w/\text{nm} \cong 0.17\omega$,²³ whilst ϕ_d determines the concentration of water droplets.

The percolation transition can be monitored by following the electrical conductivity.^{24,25} When the percolation threshold is reached, the conductivity can increase as much as four orders of magnitude. Fig. 1 shows the electrical conductivity for a pure AOT microemulsion (without BZ reactants) and for the BZ-AOT system as a function of temperature. The region of percolation is relatively wide (its width decreases with ω), and at any given temperature the conductivity is higher for the BZ loaded microemulsion (compare curves ‘W’ and ‘BZ’). The

Fig. 1 Temperature dependence of the conductivity of an AOT microemulsion loaded with BZ reactants (solid line, ‘BZ’) and pure water (dashed line, ‘W’) at $\omega = 10$, and $\phi_d = 0.45$. Concentrations of BZ reactants: [malonic acid] = 0.1 M, $[\text{H}_2\text{SO}_4] = 0.3\text{ M}$, $[\text{NaBrO}_3] = 0.25\text{ M}$, $[\text{Ru}(\text{bpy})_3^{2+}] = 0.004\text{ M}$. Inset shows conductivity–temperature plots for pure water loaded microemulsions at $\omega = 15$ and varying ϕ_d : $\phi_d = 0.56$ (black, curve 1), $\phi_d = 0.46$ (dark grey, curve 2) and $\phi_d = 0.36$ (light grey, curve 3).

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inset to Fig. 1 shows that the interval of temperature over which the percolation transition occurs depends on the droplet fraction ϕ_d at constant ω .

In a previous study of temperature-induced patterns in the bathoferroin-catalyzed BZ-AOT system, we found a new type of wave, jumping waves.²⁶ Here we show that by using temperature as a control parameter in the Ru(bpy)₃²⁺-catalyzed BZ-AOT microemulsion we are able to observe transitions from stationary Turing patterns ($T < 25$ °C) to oscillatory Turing patterns ($T = 30$ –45 °C) and eventually to traveling waves ($T > 45$ °C). Oscillatory Turing patterns, first observed in a surfactant-rich BZ-AOT microemulsion²⁷ and then in the chlorine dioxide-iodine-malonic acid reaction,²⁸ represent a combination of two very different phenomena, oscillations and stationary Turing patterns. Studies of the transitions between oscillatory Turing patterns and stationary Turing patterns, and between oscillatory Turing patterns and waves, can aid us in understanding the nature of these unusual patterns.

2. Experimental

The reactive microemulsion was prepared using the method described earlier.²⁹ Two stock microemulsions – ME1 and ME2 – were prepared, with the same droplet fraction (ϕ_d) and molar ratio ($\omega = 10$), from chemical grade aqueous BZ reagents and a 1.5 M solution of AOT (Aldrich) in octane (Aldrich). ME1 contained CH₂(CO₂H)₂ (malonic acid, MA) with H₂SO₄, ME2 contained NaBrO₃ with Ru(bpy)₃²⁺ (all Aldrich). The reactive microemulsion was obtained by mixing equal volumes of ME1 and ME2 and diluting with pure octane to give the desired droplet fraction ($\phi_d = 0.45$). After preparation, the reactive ME was kept in darkness at room temperature (23 °C) for 1 h, the induction time for the autocatalytic oxidation of Ru(bpy)₃²⁺ by NaBrO₃.³ A small drop of the reactive ME was then sandwiched between two flat windows of a dual thermostated reactor (Fig. 2). The windows were separated by a Teflon (Zefluor) membrane spacer (thickness 80 μ m, i.d. 25 mm, o.d. 47 mm). The two chambers of the reactor were threaded together with a Teflon spacer. Illumination (450 nm interference filter) from below through

Fig. 2 Reactor: (a) and (c) are thermostated chambers with sealed glass windows, where arrows indicate the direction of water flow from and to thermostated baths; (b) Teflon spacer between the two chambers. The three parts are threaded together with the reactive microemulsion (light grey) sandwiched between the chambers.

flat glass windows allowed observation from above with a microscope equipped with a charge coupled device camera (TM-7CN, Pulnix) connected to a computer. ImagePro Plus software (Media Cybernetics) was used to acquire and process image sequences.

The two chambers were thermostated at the desired temperature by continuously flowing water from a temperature-controlled bath. The water fluxes in the chambers did not cause any noticeable mechanical vibrations that might have affected patterns in the thin layer of reactive microemulsion. The temperature in the reactor was changed by switching between water fluxes from two water baths, preset at the desired temperatures at least 60 min before the experiment in order to remove air bubbles. A thermocouple in the reactor verified that the temperature change takes place almost instantaneously upon opening the water chamber.

Following an induction time of about 1 h, stationary Turing patterns form and fill the entire reactor (diameter = 2.5 cm) in approximately 10 min. In all experiments reported here, Turing patterns were allowed to fill the 23 °C thermostated reactor before further changes in temperature were made. Temperature changes in the reactor were performed as discrete jumps rather than as gradual incremental increases. Electrical conductivity measurements were recorded with a YSI 3200 conductivity instrument. Measurement of the radii of water nanodroplets by quasi-elastic light scattering was carried out with a DynaPro, Protein Solutions, High Wycombe, UK. The dynamical behaviour of the BZ-AOT system in a continuously stirred batch reactor was followed optically at a wavelength of 600 nm (the absorption maximum of the oxidised form of the catalyst) using a home-made spectrophotometric setup.³⁰ The wavelength of the stationary patterns was determined from the maximum of their 2D fast Fourier transform (FFT).

3. Results

All results reported are for a microemulsion of molar ratio 10 and droplet fraction 0.45. The concentration of the BZ reactants used in all experiments was: [MA]₀ = 0.1 M, [H₂SO₄]₀ = 0.3 M, [NaBrO₃]₀ = 0.25 M, and [Ru(bpy)₃²⁺]₀ = 0.004 M.

Fig. 3(a) shows typical Turing patterns formed at 24 ± 1 °C. These patterns emerge after *ca.* 5 min and remain stationary in time and space for up to 2 h. At lower temperatures down to 15 °C, Turing patterns persist with a similar form – see Fig. 3(b). The characteristic wavelength of the spots is the same as at 25 °C, 500 ± 20 μ m. In a well-stirred batch reactor the system displays oscillations with a period of 200 ± 20 s.

At 30 °C, the majority of the reactor maintains the presence of stationary Turing patterns, with oscillatory behaviour seen for some spots that have slightly larger (transverse) size than the other spots or stripes. The period of oscillation of these spots is 90 ± 5 s. This compares with a bulk oscillation period of 140 ± 20 s. At 30 °C most spot Turing patterns start transforming to stripes.

Fig. 4 demonstrates patterns at 35 °C. The majority of previously stationary Turing spots have now become oscillatory, with a period of 75 ± 10 s. Most spots oscillate in-phase,

Fig. 3 Stationary Turing patterns in the BZ-AOT system at (a) 25 °C and (b) 15 °C. Black corresponds to a high concentration of $\text{Ru}(\text{bpy})_3^{2+}$, white to a low concentration. $[\text{MA}]_0 = 0.1 \text{ M}$, $[\text{H}_2\text{SO}_4]_0 = 0.3 \text{ M}$, $[\text{NaBrO}_3]_0 = 0.25 \text{ M}$, $[\text{Ru}(\text{bpy})_3^{2+}]_0 = 0.004 \text{ M}$, $\omega = 10$, and $\phi_d = 0.45$. Frame size = (a) 11 mm $\times$ 5.1 mm, (b) 5 mm $\times$ 3 mm.

Fig. 4 (a) Oscillatory Turing patterns in the BZ-AOT system at 35 °C. (b) Space-time plot for the cross-section line shown in (a). Frame size = (a) 12 mm $\times$ 8 mm, (b) 7 mm $\times$ 600 s.

while some oscillate slightly out-of-phase. Spots occasionally coalesce to stripes after some time. Examples can be seen as the broader spots on the space-time plot on the left side of Fig. 5(b). The corresponding system in a stirred batch reactor displays oscillations with a period of $130 \pm 10 \text{ s}$.

At 40 °C the system supports the coexistence of several types of behaviour, *e.g.*, localized stationary Turing spots with some evidence of out-of-phase and in-phase oscillatory Turing patterns. At the same time, some parts of the reactor show new wave-like behaviour, resulting in a set of continuous inclined lines in the space-time plot (not shown). The period of oscillation of the spots is $55 \pm 10 \text{ s}$, which is roughly the same as the period of the waves. The period of bulk oscillation in a stirred tank reactor is $110 \pm 5 \text{ s}$.

At 45 °C any evidence of locally stationary (Turing) spots has gone (Fig. 5). The system now exhibits a combination of oscillatory Turing patterns with a period of $20 \pm 10 \text{ s}$ and wave-like behaviour with a characteristic wavelength of $\lambda = 1.2 \pm 0.2 \text{ mm}$ calculated as the distance between two successive waves, seen, for example, in the lower left corner of Fig. 5(a). Smaller white spots behave like oscillatory Turing patterns, while larger areas demonstrate wave-like behaviour. In general, the BZ-AOT system spends more time in the oxidised state, so the rather broad waves resemble the reduction waves found in the aqueous BZ system.³¹ The

Fig. 5 (a) Patterns in the BZ-AOT system at 45 °C. Frame size 11 mm $\times$ 7 mm. (b) Space-time plot corresponds to cross-section in (a), 9.5 mm $\times$ 200 s.

reference batch system displays oscillations with a period of about 90 s.

At 50 °C, the BZ-AOT system displays two different types of behaviour. Initially – for approximately the first 250 s after adjustment of the temperature – the system demonstrates bulk-like oscillation, superimposed over black stationary spots or short segments like that shown by the arrow in Fig. 6(a). The period of oscillation is approximately 20 s. As the BZ-AOT system is now close to the oxidised (light) state rather than the typical reduced (dark) state (seen also by the kinetics in the reference batch system), we refer to these patterns as reversed oscillatory Turing patterns.

After about 250 s the bulk oscillations slow down and develop into broad waves (period 25 s), still propagating over stationary black spots (Fig. 7). Since the system is very close to the oxidised state, these broad waves are probably reduction waves. The waves typically travel with velocity $v = 2.8 \pm 0.4 \text{ mm min}^{-1}$ and wavelength $\lambda = 1.8 \text{ mm}$. The reference batch system displays oscillations close to the oxidised state with an initial period of $50 \pm 5 \text{ s}$.

Fig. 8 shows the difference in oscillatory period between the spatially extended system and the corresponding batch system. The period of oscillation in the unstirred system is generally about half that in the stirred batch system.

Fig. 6 (a) Reversed oscillatory Turing patterns at 50 °C observed for the first 250 s. (b) Space-time plot corresponding to cross-section in (a). Frame size = (a) 11 mm $\times$ 8 mm, (b) 8 mm $\times$ 160 s.

Fig. 7 (a) BZ-AOT patterns at 50 °C, 250 s after temperature adjustment. Frame size 11 mm $\times$ 8 mm. (b) Space-time plot corresponding to cross-section in (a), 8 mm $\times$ 400 s.

Fig. 8 Dependence of period of oscillation on temperature for the stirred batch system (■, experimental; solid line to guide the eye) and the 2-D spatial unstirred patterns, including spots, stripes and waves (●, experimental; dashed line to guide the eye).

4. Discussion and conclusion

The Ru(bpy)₃²⁺-catalyzed BZ-AOT system demonstrates a wide variety of patterns.^{3,9,27} In this work we have shown that by increasing temperature as the control parameter we can induce transitions between several types of patterns: Turing

patterns → oscillatory Turing patterns → reversed oscillatory Turing patterns → reduction waves.

The characteristic wavelength of patterns can be roughly related to the diffusion length, $l_d = (D\tau)^{1/2}$, where D is the diffusion coefficient, which we approximate as $D = (D_{\text{activator}}D_{\text{inhibitor}})^{1/2}$, and τ is the characteristic time of the chemical reaction (for example, the period T of oscillations shown in Fig. 8). D increases and τ decreases with increasing temperature. In some experiments we observed coarsening of Turing patterns with an increase in temperature, while in others (like those shown in Fig. 3), the wavelength of Turing patterns remained more or less constant. This implies that l_d increases or does not change, suggesting perhaps that diffusion is either the dominant factor controlling pattern formation in this system or is compensated by decreasing τ , respectively.

The experimental evidence, *i.e.*, the dependence of the conductivity on temperature and the corresponding transition from stationary Turing patterns to waves, points toward structural changes in the microemulsion, which affect the ratio $D_{\text{activator}}/D_{\text{inhibitor}}$, as playing a more important role in the observed transitions than the inevitable increased rate of the BZ kinetics, but it is difficult to quantify this effect. We present below theoretical results that also support the view that structural effects are the key to the observed transition sequence.

From a dynamical point of view the interaction between Turing and Hopf modes is the principal reason for all the transitions found in our experiments. The Turing–Hopf interaction has been the subject of active theoretical research in recent years.^{28,32–41} The results presented here show what kinds of patterns can be found in actual experimental systems as a result of this interaction. One of these patterns, the reversed oscillatory Turing pattern, has, to the best of our knowledge, been seen here for the first time. In general, oscillatory Turing patterns can exist in two forms: in-phase and out-of-phase oscillations. Out-of-phase oscillatory Turing spots have been theoretically predicted in a number of works^{27,41,42} but have been elusive to experimentalists. Our results suggest that a regime of out-of phase oscillations exists in the $\text{Ru}(\text{bpy})_3^{2+}$ -catalyzed BZ-AOT system in the temperature range 35–45 °C. Out-of-phase behaviour is difficult to characterise precisely, however, in two-dimensional systems, where each spot may have multiple neighbours with different phases. More precise experiments in a one-dimensional configuration, *e.g.*, in a capillary tube, are desirable to confirm this conclusion.

In the neighborhood of each threshold temperature, the patterns observed above and below the transition typically coexist; *e.g.*, stationary patterns are observed with oscillatory Turing structures, and oscillatory Turing structures occur together with reduction waves. It is not clear whether this phenomenon represents true bistability or simply a transient behaviour that persists longer than the lifetime of the patterns in our batch experiments.

Further insight into our results can be gained from the two-variable model, based on the Oregonator model,⁴³ that was developed earlier for the BZ-AOT system,²⁷

$$\partial x / \partial \tau = (1/\varepsilon)[(q-x)fz/(q+x) + x(1-mz)/(\varepsilon_1 + 1-mz) - x^2] + D_x \Delta x \quad (1)$$

$$\partial z / \partial \tau = x(1-mz)/(\varepsilon_1 + 1-mz) - z + D_z \Delta z \quad (2)$$

where x and z are the dimensionless activator and catalyst concentrations, respectively; q , f , and ε are the standard parameters of the Oregonator model; and m and ε_1 are two additional parameters, with m^{-1} playing the role of the total catalyst concentration, $\Delta = \partial^2/\partial r^2$ is the Laplacian operator, and r is the dimensionless coordinate in the 1D (= one-dimensional) space.

Before presenting the results for this model we should note that it represents an extremely simple caricature of the real system. First, the model does not explicitly include such important species for pattern formation as bromine (the fast-diffusing inhibitor) and the radical BrO_2 (the fast-diffusing activator). Second, we know from our measurements of cross-diffusion coefficients in the BZ-AOT system⁴⁴ that the diffusion coefficient of the catalyst, D_z , is smaller than D_x , while in our calculations we explore the regime $D_x < D_z$. In effect, our model incorporates the transport properties of bromine in the actual system into those of the catalyst in the model. Third, this model does not take into account cross-diffusion, which is large⁴⁴ and probably significant. We also note that we do not know the true values of the model parameters nor their temperature dependences.

Model (1)–(2) is able to describe stationary and oscillatory Turing patterns, as well as reduction waves, with D_z/D_x as the bifurcation parameter. Fig. 9 presents dispersion curves (Fig. 9(a)) and a series of such patterns at one set of model parameters f , q , m , ε_1 , and ε . Fig. 9(a) shows that if D_z/D_x decreases (from 5 to 2.5), the positive maximum of the real part of the eigenvalue of the linearized system (1),(2) (associated with Turing instability) slowly decreases and becomes negative at $D_z/D_x \leq 2.67$. Stationary Turing patterns (Fig. 9(b)) are obtained for $D_z/D_x = 5$, oscillatory Turing patterns (Fig. 9(c)) at $D_z/D_x = 4$, broad waves propagating through stationary spots (Fig. 9(d) and 9(e)) at $D_z/D_x = 3.2$, and broad reduction waves (Fig. 9(f)) for $D_z/D_x = 2.5$. Fig. 9(c) demonstrates in-phase oscillatory Turing patterns, while out-of-phase oscillatory Turing patterns (with waves) are seen in Fig. 9(e). The consequences of out-of-phase oscillations at $D_z/D_x = 3.2$ can be seen in Fig. 9(d), where one full period for oscillations of each spatial point consists of two different oscillations. The period of oscillatory Turing patterns obtained in this model is 1.4 times smaller than the period of bulk oscillations, paralleling the behaviour found in our experiments and summarised in Fig. 8. By changing only the kinetic parameters, *e.g.*, ε or q , we were not able to find such a sequence of patterns, again suggesting that changes in the microemulsion structure, which affect the ratio of diffusivities, may hold the key to determining which pattern is stable at a given temperature. Of course, we can improve the agreement between the experiments and the model simulations by changing not only the ratio D_z/D_x but also the kinetic parameters, for example q and/or ε ; however, as mentioned above, we do not know how these quantities depend on temperature. It thus appears that the temperature-induced percolation transition in water-in-oil AOT microemulsions exerts a powerful influence on dissipative patterns in the BZ-AOT system.

Fig. 9 (a) Dispersion curves obtained by linear stability analysis of model (1)–(2); bold and dotted curves are, respectively, $\text{Re}(\lambda)$ and $\text{Im}(\lambda)$ at $D_z/D_x = 5, 4, 3.2$, and 2.5 (going from top to bottom curve), where λ is the eigenvalue. (b) Stationary Turing patterns at $D_z/D_x = 5$. (c) Oscillatory in-phase Turing patterns at $D_z/D_x = 4$ presented as a space–time plot with dimensions for total space = 19.5 and total time = 3.2. Panels (d) and (e) present the patterns referred to as ‘waves + out-of-phase oscillatory Turing’ at $D_z/D_x = 3.2$; (d) time behaviour of z at spatial points $r = 2.5$ and $r = 5.4$, corresponding to two neighbouring maxima of the Turing patterns; the characteristic Turing wavelength obtained from the dispersion curve in (a) is $2\pi/k_{\max} \cong 3$ ($k_{\max}$ corresponds to the maximum of the real part of the eigenvalue) which coincides well with the distance between the two chosen maxima. Black squares and white rhombs mark times at which curves 1–10 in Fig. 9(e) are taken; in (e), curves 1–5 as well as curves 6–9 are separated in time by 0.15. One full period consists of two waves. The first wave is depicted by curves 1–5 (corresponding to squares in (d)) between time $\tau = 10.35$ and $\tau = 10.95$ and induces one set of oscillatory Turing spots, while the second wave, depicted by curves 6–9 (corresponding to rhombs in (d)) between $\tau = 11.85$ and $\tau = 12.3$ induces a second set of Turing spots, which are out-of phase with the first set. Curve 10 is taken at $\tau = 13.35$ and corresponds to the last black square in (d). It is similar to curve 3. Curves 5 and 9 nearly coincide. (f) Pure reduction waves at $D_z/D_x = 2.5$. Curves 1–10 are separated in time by 0.15. Curves 1 and 10 nearly coincide. Parameters of model (1)–(2): $f = 1.3$, $q = 0.001$, $m = 250$, $\varepsilon_1 = 0.05$, and $\varepsilon = 0.03$, $D_x = 1$, $z_{\max} = 1/m = 0.004$.

Acknowledgements

This work was supported in part by the Chemistry Division of the National Science Foundation through grants CHE-0615507 and CHE-0526866 and by the Russian Foundation for Basic Research through grant 07-04-00278-a.

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