Modulation of volume fraction results in different kinetic effects in Belousov–Zhabotinsky reaction confined in AOT-reverse microemulsion

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The effects of volume fraction modulations on a Belousov–Zhabotinsky reaction catalyzed by the photosensitive Ru(bpy)₃⁺² confined in an AOT microemulsion system are analyzed. Kinetic observables such as the induction time or the initial oscillation period demonstrate two different types of correlation with the volume fraction depending on whether the system is below or above the microemulsion percolation threshold. Temporal evolution also demonstrates an exponential growth of the period with the number of oscillations independent of the volume fraction of the system.


I. INTRODUCTION

The Belousov–Zhabotinsky reaction (BZ) (Refs. 1 and 2) is one of the most studied nonlinear chemicals oscillators. This reaction-diffusion system consists of the bromination and further oxidation of an organic substrate (usually malonic acid) by bromate ions in a strongly acidic solution in the presence of a redox catalyst such as ferroin, cerium, or ruthenium bipyridyl [Ru(bpy)₃⁺²]. BZ reaction stirred in a beaker is able to display temporal oscillations and also exhibits spatiotemporal patterns in closed unstirred solutions. In order to achieve new complex structures, the BZ reaction was proposed to be confined inside water-in-oil (w/o) microemulsions (MEs) using AOT (sodium bis(2-ethylhexyl) sulfosuccinate) as the stabilizing amphiphile (BZ-AOT system). This new system demonstrates a rich variety of dynamics, some of them are impossible to be obtained in the classical BZ reaction. Cross-diffusion of the reactants was proposed as one of the possible mechanisms for pattern formation in these active microemulsions.

During the last decade, several groups have studied pattern formation in AOT microemulsion caused by external forcing, such as light effects in photosensitive reactions or sinusoidal modulation of gravity in Turing patterns. Recently, temperature has been utilized to control pattern formation in the BZ-AOT system, providing that temperature can induce changes in the physical properties of the microemulsion (specifically in the percolation transition threshold) as well as expected changes in the reaction rate constants. In the droplet interface upon the addition of homopolymers in the active media were observed to modify the expected spatiotemporal patterns.

Characteristic parameters defining the properties of the AOT reverse microemulsion such as the droplet radius and the droplet volume fraction appear as relevant factors to regulate the formation of patterns. In this regard, it was recently reported that changes in the surfactant concentration, or subsequently in the nanodroplet radius, are able to modify some features of the resulting pattern.

In this paper, we analyze the kinetic behavior of the confined BZ-AOT system by changing the volume fraction of the dispersed phase of the microemulsion keeping constant the AOT/water molar ratio. Thus, the system is able to display percolation phenomena (at a characteristic volume fraction of the dispersed phase ϕ p), in which individual spherical droplets transform into elongated water channels and induce changes of several orders of magnitude in both viscosity and electrical conductivity. We analyze whether a physical property of the microemulsion such as the percolation transition is reflected in the temporal evolution of the reaction.

II. EXPERIMENTAL

All chemicals were purchased from Sigma-Aldrich Chemical Co and used as received except octane, which was purified by mixing with concentrated H₂SO₄ for 2 days. In a typical sample preparation, a solution of 1.5 M AOT in octane was used to make two different AOT MEs with different aqueous content. The first microemulsion (ME₁) was composed of malonic acid (MA) and H₂SO₄, while the second one (ME₂) was loaded with a 20 mM of Tris(2,2′-bipyridyl) dichlororuthenium (II) hexahydrate [Ru(bpy)₃]⁺² and sodium bromate. Both stock microemulsions ME₁ and ME₂ were prepared at the same droplet volume fraction, ϕₚ (0.68) and with the same droplet size, obtained through the relation ω ≡ [H₂O]/[AOT] = 12.32.

The reactive microemulsion was obtained by mixing equal volumes of both stock microemulsions (ME₁ and ME₂) and subsequently diluted with octane until achieving the

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desired droplet concentration. The concentration of BZ reactants in the aqueous phase was \([\text{MA}]_0 = 0.25 \text{ M}, [\text{H}_2\text{SO}_4]_0 = 0.25 \text{ M}, [\text{NaBrO}_3]_0 = 0.16 \text{ M}, \text{and } [\text{Ru(bpy)}_3^{2+}]_0 = 4 \text{ mM}.\)

Dynamic light scattering (DLS) measurements were performed with a laser light scattering instrument with vertically polarized incident light (\(\lambda = 488 \text{ nm}, 2 \text{ W argon ion laser, Coherent Inc., Santa Clara, CA)}\) combined with a digital correlator (ALV 5000E, ALV GmbH, Germany). All solutions were previously filtered with 0.2 \(\mu\text{m} PTFE \text{ filter membranes (Millex, Millipore Inc. USA). DLS correlation data were analyzed by the constrained regularized CONTIN method to obtain distributions of decay rates.}\)

The hydrodynamic radius \(r_h\) was estimated from the diffusion coefficient using the Stokes–Einstein equation (\(D_0 = k_BT/6\pi r_h\eta\)) where \(D_0\) is the diffusion coefficient of a sphere at infinite dilution, \(k_B\) the Boltzmann constant, \(T\) the absolute temperature, and \(\eta\) the solvent (octane) viscosity.

Conductivities were measured on a Mettler Toledo SevenEasy Conductivity meter at room temperature using an in-Lab 730 measuring cell. Spectrophotometric measurements were carried out in 3.5 ml continuously stirred cuvettes with a Vernier spectrometer (Ocean Optics) connected with a computer where the data were analyzed through LOGGER PRO software. In all the experiments the stirring rate was kept constant. Moreover, in order to reduce uncertainties, data displayed were average of three different experiments.

III. RESULTS

Electrical conductivity measurements were required to analyze whether the percolation transition is achieved by changing the volume fraction of the dispersed phase. The anionic AOT microemulsion loaded with all the BZ reactants shows an increase in the conductivity of 2 orders of magnitude with increasing volume fraction of the dispersed phase (Fig. 1). We estimated the percolation threshold of the BZ-AOT system around \(\phi_p = 0.5\). It is important to note that the electrical conductivity is mainly caused by the mobility of the charged carriers, this is, AOT anions (\(\sigma_{\text{AOT}}\)) and the ions dissolved into the aqueous phase (\(\sigma_{\text{water}}\)). Na counterions plus ions generated in the course of the BZ reaction, so \(\sigma = \sigma_{\text{AOT}} + \sigma_{\text{water}}\). Nevertheless, usually in water-in-oil AOT microemulsions the electrical conductivity is almost entirely due to sodium counterions in the water phase, since the mobility of the cation species is much greater than that of the AOT anion. By using the same reasoning, we will consider \(\sigma \approx \sigma_{\text{water}}\) once the BZ reaction is confined into the AOT microemulsion.

In order to characterize the BZ-AOT system, we performed DLS experiments at different sample dilutions. It is necessary to point out that these experiments were made in the absence of ruthenium to avoid light scattering due to solution coloration. The main results are shown in Fig. 2. We distinguish two different population distributions depending on the volume fraction of the dispersed phase in relation to the critical percolation threshold (\(\phi_p = 0.5\)). Samples below percolation (\(\phi < \phi_p\)) display a main peak centered at ca. 2–3 nm, in fair agreement with the droplet size predicted by using the well-known approximated relation \(R = 0.175 \omega (r_h = 2 \text{ nm}).\)

As the volume of the dispersed phase is increased, the percolation transition is reflected through a shift in the droplet population to a bimodal distribution (see Fig. 2). Meanwhile the peak at 2–3 nm remains unaltered, a second peak appears with a characteristic size almost 1 order of magnitude greater. This larger hydrodynamic radius is associated with the formation of water channels that span the microemulsion, meanwhile the smaller one represents the presence of individual droplets.

The kinetics analysis of the BZ-AOT system was performed through a spectrophotometer at different volume fractions of the dispersed phase in a continuously stirred reactor at room temperature. Figure 3(a) demonstrates the typical evolution of our active medium. The BZ-AOT reaction has an induction period (IP) to initiate the autocatalytic oxidation of Ru(bpy)_3^{2+} by NaBrO_3. The reaction starts to oscillate with a characteristic initial period (\(T_0\)), which demonstrates an important temporal dependence. At this stage, it is necessary to mention that in spite of that both of the kinetic observables (IP and \(T_0\)) change with the droplet concentration as previously reported, in this paper we try to perform a quantitative study of such dependence.

Dimensionless units were proposed to highlight the variation of the BZ-AOT characteristics with volume fraction dilution. Taking into account that \(T_0, \text{ and } IP\) are the values associated with the most diluted samples, we rescaled our observables as \(T_0' = T_0/ T_0, \text{ and } IP' = IP / IP\). Since the system needs some time to start the autocatalysis, it is reasonable to expect that the induction time will depend on the microemulsion parameters. In this regard, Fig. 3(b) shows the dependence of the dimensionless induction time with the

\[\text{FIG. 1. Conductivity measurements of the AOT microemulsion loaded with the entire BZ reactants at } \omega = 10 \text{ for different volume fractions of the dispersed phase.} \]
electrical conductivity of the microemulsion system for each volume fraction of the dispersed phase. Figure 3(b) proves that $\text{IP}'$ decreases in a different manner depending on whether the analysis is performed above or below the percolation transition. Thus, the critical conductivity ($\theta_p$) associated with $\varphi_p$ is inserted to make easier the comprehension of Fig. 3(b). In this way, if $\theta < \theta_p$, the dimensionless induction period sharply diminishes with conductivity, with values up to half of $\text{IP}_{\text{max}}$ for the range between 4 $\mu$S/cm $< \theta < 10$ $\mu$S/cm; meanwhile, when $\theta > \theta_p$, $\text{IP}'$ smoothly decreases across the variation of 2 orders of magnitude in conductivity data.

Dimensionless initial period of oscillation ($T_0'$) also presents a complex correlation with the volume fraction of the system. The dependence of $T_0'$ with the conductivity is...
FIG. 4. (a) Evolution of the period of oscillation with the number of oscillations that displays the BZ-AOT system at $\varphi = 0.48$. (b) Dimensionless evolution of period for two different dilutions of the system: $\varphi = 0.67$ (squares) and $\varphi = 0.36$ (circles). Both samples demonstrate the same temporal evolution, independent of the dilution of the system.

also presented in Fig. 3(b). Below percolation ($\theta < \theta_p$), $T_0'$ demonstrates an important decrease, reaching values almost three times smaller than $T_{0,\text{max}}$. On the other hand, analysis of samples above the percolation threshold shows a slightly decrease in the dimensionless initial period. Thus, in the range of conductivity studied (10 $\mu$S/cm $< \theta < 10^3$ $\mu$S/cm), we observed only a 15% of variation in $T_0'$. We relate the variation in the kinetic observables ($T_0'$ and IP') to the diffusion mechanisms occurring in the BZ-AOT system. Taking into account that the BZ reaction takes place through the exchange of material between droplets, the so-called exchange diffusion coefficient, as defined by Kataoka et al.\textsuperscript{37} can be considered:

$$D_{\text{exchange}} = D_{\text{water}} - D_{\text{droplet}},$$  \hspace{1cm} (1)

where $D_{\text{water}}$ is the water diffusion coefficient, which is the main contributor for conductivity values; $D_{\text{droplet}}$ corresponds with the droplet diffusion coefficients, which can be easily derived through the hydrodynamic radius obtained by DLS measurements, as we previously shown in Fig. 2. The reaction-diffusion process presents both the largest induction time and initial period for the most diluted samples (i.e., lower volume fractions). The increase in volume fraction to larger values (experimentally associated with a reduction of the oil phase) involves a larger probability of exchanging material (the BZ reactants). This phenomenon can be explained in terms of the antagonist behavior of the diffusion coefficients: for samples below the percolation transition, $D_{\text{droplet}}$ should remain constant since there is no change in the droplet radius; in contrast, $D_{\text{water}}$ would increase as the conductivity does. Thereby, there is a magnification in the exchange diffusion coefficient as we increase the volume fraction and, consequently, this would be reflected in faster $T_0'$ and IP', in agreement with previous reports.\textsuperscript{39} Also, by additional increases of the volume fraction, the BZ-AOT system reaches the percolation transition, which involves an even much faster exchange of reactants, either through the formation of droplet clusters (dynamic percolation) or the coalescence of the droplets into water channels (static percolation).\textsuperscript{40} In this regard, AOT microemulsions have shown different ways of percolation\textsuperscript{41} by just changing the counterions from (Na$^+$) to Ca$^{2+}$. This demonstrates the high sensitivity of AOT microemulsion to the presence of different species in solution. For volume fractions values well above the percolation transition ($\varphi \gg \varphi_p$), we assume that the exchange of BZ reagents is mainly due to static percolation, as occur for temperature-induced Na-AOT percolation.\textsuperscript{18} It is also necessary to bear in mind that above percolation single-dispersed spherical droplets are still present, as previously observed in Fig. 2. Hence, once the active microemulsion reaches the percolation state, there exist an additional contribution to the conductivity due to the collision of the remaining droplets with the water channels,\textsuperscript{37} which corresponds with a smoothly modification in the kinetic features.

The evidence of intermicellar exchange of reactants ($D_{\text{exchange}}$) has been thoroughly studied in the past for AOT water-in-oil microemulsions,\textsuperscript{42, 43} and we consider it as the main responsible for the BZ-AOT system. However, in the literature other models are developed in order to explain the interaction of droplets and subsequently the solute exchange,\textsuperscript{31} by either introducing the stickiness between droplets as a scaling quantity\textsuperscript{44} or considering the compartments as hard spheres.\textsuperscript{45} For example, by including a reaction-diffusion in a heterogeneous milieu, such as the BZ-AOT system, Alonso et al. consider an effective medium theory\textsuperscript{46} with two well differentiated domains, which depend on the volume fraction and the spatial dimension of the system.\textsuperscript{47} The development of these modelizations can be a good tool to obtain a better
understanding of the complex BZ-AOT system and their variety of spatiotemporal dynamics.

On the other hand, we analyzed the correlation between the kinetic observables of the active media ($T_0^*$ and IP) for the respective volume fraction. Thus, Fig. 3(c) demonstrates a linear dependence between the induction time and the period of the oscillation. This result highlights that both features exhibit the same tendency for the entire droplet volume fraction analyzed.

In order to characterize the temporal behavior of the BZ-AOT system, we analyze the evolution of the period of the system. Thus, we observe how the initial characteristic period ($T_0$) changes drastically in the course of reaction, exhibiting an exponential dependence with the number of oscillations the system may display [Fig. 4(a)]. Dimensionless units were used for a better understanding of the temporal evolution of the period of oscillation. We name $T' = 1/T_0$, where $T$ is the instantaneous period at time $t$ and $T_0$ is that corresponding at the initial oscillation, respectively. Temporal analysis, at different volume fractions, demonstrates that the evolution of the oscillation period is independent of the dilution of the system, with the same slope for samples above or below the percolation threshold.

IV. CONCLUSIONS

The relevance in the characterization of different kinetic observables of the BZ-AOT reaction-diffusion system is highlighted with the addition of a photosensitive catalyst, as Ru(bpy)$_3^{2+}$. In this way, the knowledge of the induction time or the period of oscillations plays an important role in the control of the different spatiotemporal patterns that are possible under the application of an external forcing as light.

Here, we discuss the effect of the dilution of the AOT microemulsion without performing any change in the BZ reaction. In order to restrict the system, the radius of the nanodroplets remains constant for any value of volume fraction below percolation. Thus, an increase in the volume fraction is produced by a reduction in the continuous oil phase, leaving the dispersed phase unaltered.

Dependence of the kinetic characteristics, IP and $T_0$, on volume fraction demonstrates their similar qualitative correlation. Mainly, BZ-AOT kinetic characteristics are shortened as we increased the volume fraction of the active microemulsion. Below the percolation threshold, IP and $T_0$ demonstrate the largest reduction associated with the reduction of the oil phase. Once the system reaches the percolation transition, the kinetic features diminish smoothly with the volume fraction, result observed along 2 orders of magnitude in conductivity data. The evolution of the period of oscillation displays an exponential growth with time. Analysis for samples above and below percolation demonstrates the evolution of the oscillation is independent of the droplet volume fraction.

The experimental data were explained by considering that the water diffusion coefficient in the AOT microemulsion is smaller than in bulk water and can be derived through the addition of the droplet and exchange diffusion coefficients.

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