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New features in the dynamics of a ferroin-catalyzed Belousov–Zhabotinsky reaction induced by a zwitterionic surfactant

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Abstract

Interactions between reaction-diffusion systems and aggregated host environments are a subject of widespread interest. In this work, the behavior of the Belousov–Zhabotinsky reaction was investigated in a micellar environment formed by the zwitterionic surfactant N-tetradecyl-NN-dimethylamino oxide (C14DMAO). The appearance of an induction period with a threshold-like dependence upon the surfactant concentration, was detected at [C14DMAO] \( \approx 5 \times 10^{-3} \) mol dm\(^{-3}\). These new features were explained in terms of the segregation ability typical of the amphiphilic self-assembling systems. Numerical simulations were also performed to confirm the proposed mechanism.

1. Introduction

The Belousov–Zhabotinsky (BZ) reaction, initially proposed as a simplified scheme of a metabolic pathway (Krebs cycle) [1], was subsequently adopted as a more general model for certain major nonlinear phenomena, e.g. enzymatic catalysis, biological oscillations and pattern formation [2–4]. The BZ reaction, in its most used formulation, consists in the catalytic oxidation of malonic acid (MA), by bromate ions in a strongly acidic aqueous solution [5]. Metal redox couples such as Ce(IV)/Ce(III) or ferriin/ferroin (Fe(phen)\(^{3+}\)/Fe(phen)\(^{2+}\)), are often used as catalysts.

Several authors [5–7] pointed out the different behavior between cerium and ferroin-catalyzed BZ systems, in particular the absence of a pre-oscillatory induction period (IP) for the latter (even if under certain experimental conditions, IP appears also for ferroin systems [8–10]), and a different dependence of the oscillation frequency upon the relative initial concentrations of reactants. The pre-oscillatory induction period is the typical single length oscillation at the start of the cerium-catalyzed BZ system [5]. During the IP, the Br\(^{-}\) concentration is increased and brominated organic species are accumulated. According to the GTF model [11] the length of IP is determined by the concentration of bromomalonic acid (BrMA). The crucial amount of BrMA necessary for the onset of oscillations is produced through two main pathways: (a) the bromination of the enol form of malonic acid by Br\(_2\) and (b) the reaction between Br\(_2\) and the malonyl radical formed in the Ce-MA subsystem [12].

The oxidation potential of the redox couple ferriin/ferroin is significantly lower than the couple Ce(IV)/Ce(III) and this is the main reason accounting for the differences in the two oscillating systems. Various hypothesis have been proposed to explain the reactivity of the ferroin toward the organic substrates, in particular it was postulated that ferroin could react only with bromomalonic acid. Recently, Noszticzius and coworkers [13] unambiguously proved that ferriin does not react with malonic acid, thus preventing the bromide formation through the aforementioned reaction pathway (b). Due to the low redox potential of the catalyst couple, the reaction of ferroin with the oxybromine species has been identified as an alternative Br\(^{-}\) source [5,14], according to the following reaction scheme:

\[
\begin{align*}
2\text{Fe(phen)}^{2+} + \text{BrO}_3^- + 3\text{H}^+ & \rightarrow 2\text{Fe(phen)}^{3+} + \text{HBrO}_2 + \text{H}_2\text{O} \quad \text{(B1)} \\
2\text{Fe(phen)}^{2+} + \text{HBrO}_2 + 2\text{H}^+ & \rightarrow 2\text{Fe(phen)}^{3+} + \text{HOBr} + \text{H}_2\text{O} \quad \text{(B2)} \\
2\text{Fe(phen)}^{2+} + \text{HOBr} + \text{H}^+ & \rightarrow 2\text{Fe(phen)}^{3+} + \text{Br}^- + \text{H}_2\text{O} \quad \text{(B3)} \\
2\text{Fe(phen)}^{2+} + \text{Br}_2 & \rightarrow 2\text{Fe(phen)}^{3+} + 2\text{Br}^- \quad \text{(B4)}
\end{align*}
\]

The combination of a chemical oscillator with confined reaction environments is a subject extensively studied during the past years. Among the others, surfactant forming micelles (direct and reverse) revealed to be very fascinating and promising [15–23]. The so-called direct micelles are formed by the spontaneous clustering of amphiphilic molecules to give aggregates where the hydrophobic moieties are segregated from the outer hydrophilic environment. One of the most important properties of micellar solutions is their ability to selectively interact with the reacting substrates present in the medium, depending on their chemical proprieties (e.g. charge and/or hydrophobicity) [24,25].

Following our previous works [16,17,19,20] about chemical oscillators and surfactants, in this Letter we focus on the dynamics of the ferroin-catalyzed BZ system perturbed by using a peculiar and versatile zwitterionic surfactant; namely, N-tetradecyl-NN-dimethylamino oxide (C14DMAO), in a stirred batch reactor. C14DMAO has been classified between the cationic and purely...
nonionic surfactants [26], and, like others n-alkyldimethylammonio-
dides, it has the capability to form large rod-like micelles with
lengths of several thousand Angströms in the presence of electro-
lytes [26,27].

2. Experimental

Malonic acid, sodium bromate, sodium bromide, sulfuric acid
and ferroin (Fe(o-phen)_3SO_4) were commercial grade reactants
(Fluka). C_{14}DMAO (chemical structure shown in Fig. 1) was a gift
of Prof. H. Hoffmann (Bayreuth Center for Colloids & Interfaces).
All chemicals were used without further purification. Stock solu-
tions were prepared by weight before use. Deionized water from
reverse osmosis (Elga, model Option 3), having a resistivity higher
than 1 MΩ cm, was used to prepare all solutions.

Samples for the kinetics runs were prepared in spectropho-
tometric quartz cuvettes (1 x 1 x 5 cm) diluting and gently stirring
a solution containing the BZ components, except ferroin, with dif-
fident amount of C_{14}DMAO stock solution (0.20 mol dm^{-3}). Oscilla-
tions were started by adding ferroin. Finally, cuvettes were placed
in a UV–Vis spectrophotometer (Beckman DU-640, equipped with
thermostatted compartments and a magnetic stirring apparatus)
for data acquisition. The initial concentrations of the BZ reactants
in the mixture were: [MA] = 0.03 mol dm^{-3}, [NaBrO_3] = 0.12
mol dm^{-3}, [ferroin] = 5.0 x 10^{-4} mol dm^{-3}, [H_2SO_4] = 0.30 mol dm^{-3}
and [C_{14}DMAO] was varied in the range 0–9.0 mol dm^{-3}.
Time series were recorded following the absorbance of ferroin at
a wavelength \lambda = 510 nm where the ferroin molar extinction coef-


cient \epsilon = 1.1 x 10^{4} mol^{-1} dm^{3} cm^{-1}.

The critical micelle concentration (c.m.c.) of C_{14}DMAO in aque-
sous solutions was estimated as the intersection point of the two
linear plots, above and below the c.m.c., of the surface tension ver-
sus log of surfactant concentration.

Surface tension values were determined both in the absence
and in the presence of BZ reactants at the concentrations used
for experiments. Measurements were carried out by means of a
KSV-Sigma 70 automatic tensiometer by using the Whilelmy plate
method. The c.m.c. value in the presence of BZ reactants was
6.3 x 10^{-3} mol dm^{-3}. The lower value with respect to that in water
(1.6 x 10^{-4} mol dm^{-3}, which is in complete agreement with that
reported in the literature [26]) is in line with the effect caused
by the presence of added electrolytes.

All measurements were performed under constant stirring at
20.0 ± 0.1 °C.

The oscillation period τ, has been evaluated as the temporal dif-
ference between successive peaks from the time series recorded
spectrophotometrically. In particular, we refer to \tau_{0}, which repre-
sents the mean period of the first 6 min of oscillations. All oscilla-
tion parameters with relative errors were calculated from five
different experimental runs.

3. Results and discussion

The influence of C_{14}DMAO on the dynamics of the ferroin-cata-
yzed BZ reaction was investigated over a wide surfactant concen-
tration range. The analysis of the experimental timeseries showed
that in the surfactant concentration range 0 < [C_{14}DMAO] < 5.0 x 10^{-3}
mol dm^{-3}, both the qualitative and the quantitative profiles of the
absorbance as a function of time, were substantially unchanged with
respect to that in the absence of surfactant. When a critical concen-
tration of [C_{14}DMAO]_{cr} = 5.0 x 10^{-3} mol dm^{-3} was reached a new
feature in the dynamics appeared, namely an induction period
before the oscillating regime (Fig. 2).

As mentioned in Section 1, the presence of the pre-oscillatory
stage in a ferroin-catalyzed BZ system is quite surprising. In pre-
vious experiments with an anionic surfactant (sodium dodecyl sul-
phate, SDS) [20], we did not observe similar effects; conversely
we found that negatively charged micelles induced an acceleration
of the oscillatory dynamics. Paul [18] found that an IP appeared
when BZ was conducted in positively charged micelles (cetyltri-
methylammonium bromide, CTAB), while the dynamics were com-
pletely changed in the presence of nonionic or zwitterionic
surfactants.

The dependence of the IP length upon the surfactant concen-
tration is depicted in Fig. 3. Since the IP shows a threshold-like depen-
dence on the surfactant concentration, [C_{14}DMAO] could be
considered a bifurcation parameter for the reaction dynamics. This
fact suggests a strong interaction between the surfactant and one
or more of the chemical species crucial for the temporal evolution
of the BZ reaction.

Beyond the critical value \[C_{14}DMAO]_{cr}, the length of the induc-
period was found to vary with \[C_{14}DMAO]. In particular, after

![Fig. 1. Chemical structure of C_{14}DMAO.](image-url)

![Fig. 2. Comparison between a BZ reaction in the absence (A) and in the presence of \([C_{14}DMAO] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}\) (B) at 20.0 °C. For both systems the following initial reactants concentrations were used: \([MA] = 0.03 \text{ mol dm}^{-3}, [NaBrO_3] = 0.12 \text{ mol dm}^{-3}, [ferroin] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}, [H_2SO_4] = 0.30 \text{ mol dm}^{-3}\) and \([C_{14}DMAO]_{cr} = 5.0 \times 10^{-3} \text{ mol dm}^{-3}\). The absorbance of ferroin was measured at \lambda = 510 nm.](image-url)

![Fig. 3. Dependence of the IP upon the concentration of C_{14}DMAO. At \([C_{14}DMAO] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}\) the system undergoes a bifurcation and an induction period appears.](image-url)
an increase, it seems that the IP value tends to attain a plateau. Unfortunately, we could not perform experiments above 
[C14DMAO] = 0.05 mol dm−3, due to the high viscosity of the solutions.

We also performed several experiments in the narrow interval 
4.0 · 10−3 < [C14DMAO] < 5.0 · 10−3 mol dm−3. We could not find a 
defined induction period in this region; the relaxation 
ocillations during the first 400–500 s were randomly staggered 
by fast oscillations with very small amplitude or intervals where 
ocillations were completely damped (Fig. 4A). Fig. 4B shows the 
dependence of the oscillation period τm upon the surfactant concentration. 
Perusal of this figure reveals that τm is not as sensitive 
as the IP to the presence of the micelles in solution, and its behavior 
does not dramatically change. Actually, τm seems to slightly 
decrease beyond the c.m.c. (~90 ± 75 s), but after this value it is no 
more sensitive to the surfactant concentration increase. In fact, the 
small variation before and after [C14DMAO]c.m.c. are within the 
experimental error.

The different behavior manifested by the IP and τm, is of crucial 
help in understanding how the presence of the surfactant influences 
the BZ reaction dynamics. A sensitivity analysis [28] showed that the most important step in determining the oscillation period of the BZ reaction is the oxidation of the organic substrate by the 
catalyst to regenerate bromide (Process C in PKN model [29]). In the 
ferroin-catalyzed system process C is

\[
2\text{Fe(phen)}^3+ + \text{BrMA} \rightarrow f\text{Br}^- + 2\text{Fe(phen)}^2+ + \text{other products}
\]

The fact that τm is not significantly altered by the presence of the 
surfactant suggests that the catalyst is not located in the micellar 
pseudophase, but it is confined in the aqueous one. We confirmed 
this hypothesis by performing a spectrophotometric analysis of the 
ferroin decomposition reaction rate:

\[
\text{Fe(phen)}^2+ + 3\text{H}^+ \rightarrow \text{Fe(II)} + 3\text{phen} \text{H}^+
\]

The first order rate constant was found to be 8.3 ± 0.5 · 10−3 s−1 
both in the absence and in the presence of the surfactant at various 
concentrations. Moreover the peak shape of the ferroin remained 
unchanged in the micellar medium. These evidences allowed us to 
rule out any interactions, either electrostatic or hydrophobic, be- 
tween the ferroin and the aggregated system and suggested that 
others key species have to play a relevant role.

Bromine is involved in pathway (a) responsible for the induc- 
tion period (see Section 1); its role in BZ/micelles systems was 
investigated in our previous works and evidences for the Br2 solu-

bilation in different type of aggregated systems were given ([19] 
and references therein). For the BZ/C14DMAO system, preliminary 
experiments showed a strong association between Br2 and the 
micellized surfactant. This is coherent with the high hydrophobicity of the 
molecular halogen, which tend to move in the non-polar 
pseudophase inside the micelles. In fact, from spectrophotometric 
measurements, it was found that by mixing the molecular bromine 
with different aqueous zwitterionic solutions, a new absorption 
bond with a maximum at λ = 271 nm appeared. At high concentra-
tion of both Br2 and C14DMAO the formation of a yellowish adduct 
was also detected. In order to evaluate the influence of bromine on the 
IP, we decided to monitor the response of the BZ/C14DMAO sys-
tem by forming Br2 in situ. This was achieved by adding an increas-
ing amount of NaBr to different solutions at [C14DMAO] = 
5.0 · 10−3 mol dm−3. The added bromide reacts with BrO3− according 
to the stoichiometry:

\[
\begin{align*}
\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ & \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O} \quad (3) \\
\end{align*}
\]

developed. We performed numerical 
simulations by combining reactions (B1)–(B4), (E1) and (E2) with

\[
\begin{align*}
\text{CH}_2(\text{COOH})_2 &= (\text{COOH})\text{CH(OC)H}_2 & (\text{E1}) \\
\text{(COOH})\text{CH(OC)H}_2 + \text{Br}_2 & \rightarrow \text{BrCH(OC)H}_2 + \text{H}^+ + \text{Br}^- & (\text{E2})
\end{align*}
\]

during the samples preparation, NaBr was added to the BZ mixture 
before the catalyst; oscillations were then started by adding the 
ferroin only after that the typical brown-red color of bromide disap-
pear from the solution.

Fig. 5 shows how the concentration of added bromide, and conse-
quentially of Br2 and BrMA, influences the length of the induction 
period. A confront against Figs. 3 and 5 reveals an almost specular 
spatial behavior of the induction period toward the presence of the surfa-
tant and of the bromide, respectively. In fact, increasing the 
amount of bromide in solution leads to a decrease in the induction 
period length and eventually to a new bifurcation after which the 
IP completely disappears.

In order to further test our mechanistic hypothesis, we also 
simulated the observed behavior of the BZ/C14DMAO system. As men-
tioned in Section 1, the mechanism of a ferroin-catalyzed BZ 
reaction is not well understood, and, to the best of our knowledge, 
models that reproduce quantitatively all the characteristics of the 
system, have not yet been developed. We performed numerical 
simulations by combining reactions (B1)–(B4), (E1) and (E2) with

\[
\begin{align*}
\end{align*}
\]
a standard model for the ferroin-catalyzed BZ reaction [30], which we already used to simulate the BZ/SDS system [20].

Generally, reactions (E1) and (E2) are not included in the ferroin-catalyzed BZ models. Recently [9,10], their contribution has been successfully integrated with the oregonator model [31,32] to emphasize the role of the bromide ions as bifurcation and control parameter. In such a way it was also possible to explain the reduced induction phase before the appearance of waves in the unstirred ferroin-catalyzed systems.

To account for the interaction between the bromine and the surfactant we inserted the equilibrium reaction:

\[ \text{C}_{14}\text{DMAO} + \text{Br}_2 \rightleftharpoons \text{C}_{14}\text{DMAO} - \text{Br}_2 \]  

we chose the constants for reaction (4) in order to get a ratio between the forward and the reverse constant roughly equal to 2000. A similar value was calculated for the interaction of bromine with the surfactant sodium bis(2-ethylhexyl)sulfosuccinate (AOT) [33].

All constants were taken from the literature (Ref. [14] for reactions (B1)–(B4), Ref. [34] for reactions (E1) and (E2) and Ref. [30] for the rest), except those for the reaction between ferrion and bromomalonic acid which were chosen with an optimization procedure to fit the experimental data. Numerical integration was performed by using COPASI package [35].

Our simple model is able to reproduce in a qualitative way all the new features induced in the dynamical behavior of the BZ reaction by the presence of the surfactant. Moreover, for a low concentration of C14DMAO and/or added NaBr, also a good quantitative accordance between simulations and experimental results was obtained. As an example, we report in Fig. 6 the simulation relative to the progressive addition of NaBr in solution, when \([\text{C}_{14}\text{DMAO}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}\). The threshold value at which the induction period disappears is significantly lower in simulations respect to the experimental value (1.1 \times 10^{-3} \text{ mol dm}^{-3} versus 4.0 \times 10^{-3} \text{ mol dm}^{-3}), nevertheless at low NaBr concentrations, a good agreement between the two trends was found.

Two aspects should be taken into account to explain the discrepancies between experiments and simulations: (i) In our experimental condition the amino-oxy group of the surfactant is protonated, therefore the micelles have mainly a cationic character. In these conditions, reactions between anionic species can be significantly influenced. For example, reaction 3 was found to respond in a nontrivial way in the presence of a zwitteronic [36] or a cationic [37] micellar system. (ii) C14DMAO micelles are known for their ability to change shape depending on the surfactant concentration [26], thus influencing the hydrophobicity of the system. This aspect can also contribute to explain the threshold-like dependence of the IP upon the surfactant concentration.

4. Concluding remarks

In this Letter, we showed how in the dynamics of the ferroin-catalyzed Belousov–Zhabotinsky oscillating system, new features appear upon the addition of increasing amount of the zwitterionic surfactant C14DMAO, in stirred closed reactors. In particular, an induction period similar to the pre-oscillatory stage typically manifested by the cerium-catalyzed reaction, was detected. The IP was also found to manifest a threshold-like dependence on the surfactant concentration. The observed trends have been ascribed to the segregation ability typical of the amphiphilic self-assembling systems, which we demonstrated to strongly interact with brominated species. Simulations showed that simply taking into account the interaction of Br2 with C14DMAO, it is possible to qualitatively reproduce the observed features. Further structural and kinetic studies are in progress to improve the accuracy between the experiments and the model.

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