The Effect of Sodium Dodecylbenzenesulfonate (SDBS) Micelles on a Belousov-Zhabotinsky Oscillating System Catalyzed with a Tetraazamacrocyclic Copper(II) Complex

by Yang-Yang Chen^a), Gang Hu^{*a}), Yu-Qin Nian^a), Meng-Shuo Li^a), Ji-Mei Song^a), and Lin Hu^b)

a) Department of Chemistry, Anhui University, Hefei 230601, P. R. China $(phone/fax: +86-551-63861279; e-mail: [hugg@ustc.edu\)](mailto:hugg@ustc.edu)$ b) Institute of Applied Chemistry, East China Jiaotong University, Nanchang 330013, P. R. China

This article deals with the influence of micelles of the anionic surfactant sodium dodecyl benzene sulfonate (SDBS) on the *Belousov–Zhabotinsky* (*B–Z*) oscillating reaction catalyzed by a tetraazamacrocyclic copper(II) complex $\lceil \text{CuL} \rceil \cdot \text{Cu}_2 \rceil$, an enzyme-like catalyst (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene). Unlike the classical B-Z oscillator in which malonic acid is usually used as a substrate, malic acid (an intermediate in the Krebs cycle) is involved in this oscillating system. Experiments reveal that formation of the SDBS micelles markedly affects the behavior of the oscillating reaction. It is found that there is a linear relationship between the change in the oscillation amplitude (ΔA) and the concentration of SDBS, whereas the change in the oscillation period (ΔT) is linearly proportional to the SDBS concentration. The most likely mechanism that involves the formation of the SDBS micelles and the effects of the micelles on the oscillating chemical system can be rationalized by assuming that the SDBS micelles are so negatively charged that they attract more $[CuL]$ ³⁺ than $[C\text{u}L]^{2+}$. This hypothesis was confirmed by UV/VIS spectrophotometric measurements of a constant concentration of $\text{[CuL]}(\text{ClO}_4)_{2}$ in different concentrations of SDBS; as the SDBS concentration increased, the absorbance of $\lceil \text{CuL} \rceil \cdot \text{CuQ}_2 \rceil$ increased, while the maximum absorption wavelength for $[CuL] (ClO₄)₂$ remained at 502 nm.

1. Introduction. – Oscillating chemical reactions, in which periodic changes in the concentrations of certain chemical intermediates occur in time or in space, have been adopted not only as general models for non-equilibrium phenomena [1] [2] but also as ideal matrixes for biological oscillations and pattern formation [3]. Among the various chemical oscillators [4][5], the *Belousov–Zhabotinsky* $(B-Z)$ oscillating systems are more well-known and more thoroughly studied than other systems, such as the Briggs–Rauscher (B–R) and Bray–Liebhafsky (B–L) oscillators. Moreover, B–Z oscillators are the simplest systems that show complex behavior, and this simplicity makes the oscillators ideal matrices for use in mimicking the mechanisms of a number of biological processes [6].

In an effort to select suitable $B-Z$ systems with different components as ideal models for mimicking bio-oscillation, it has been assumed that the components in the B-Z oscillator should not only include biologically active substrates (e.g., malic acid) but enzyme-like catalysts as well. Recently, however, the catalysts involved in most B-Z oscillating systems have been metal ions such as manganese ions, cerium ions, etc. [7]. Few reports have been published on enzyme-like catalysts (such as the

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tetraazamacrocyclic complex); and hardly any experiments have been performed on the use of bioactive molecules as organic substrates. Nevertheless, in our previous studies, we have established some novel $B-Z$ oscillating systems $[8-12]$ that not only use tetraazamacrocyclic complexes [13] as catalysts (enzyme-like catalysts) but also involve intermediates of the *Krebs* cycle (pyruvic and malic acid) as substrates. These species make such oscillators of potential interest in studies that mimic biochemical oscillations.

In addition to searching for new oscillators of biological interest, the coupling of oscillating reactions with peculiar reaction environments has attracted the attention $[14-16]$. Some examples include the combination of B-Z systems with microemulsions [17], vesicles [18], and micellar media [19], or the binding of B-Z systems to gels [20]. Studies on the B-Z system in micellar media seem to be more promising, because surfactants aggregate to form micelles, which have the ability to selectively bind or even selectively react with the species present in the medium. The selectivity, which arises from the different structures of the electrically charged micelles, plays an important role in controlling the kinetic steps in the B-Z oscillation.

Recent studies on the effects of micelles on the $B-Z$ reaction focus on some interesting oscillatory behaviors that the $B-Z$ reaction has exhibited under the influence of micelles, such as the mechanism of the kinetic effects [21], spatio-temporal perturbation [22], change in oscillatory behavior [23], etc. For example, Cavasino et al. observed that aggregation of the cationic surfactant cetyl(trimethyl)ammonium nitrate (CTAN) can affect the oscillation period and duration, while they investigated the effects of micelles on the Ce-catalyzed $B-Z$ reaction [19]. In 2001, *Biswas et al.* published a treatise discussing inhibitory effects on $B-Z$ oscillations in the bromate, oxalic acid, MnSO₄, H₂SO₄, and acetone system [24]. The behavior of the ferroincatalyzed B-Z reaction was assessed in a micellar environment formed with a zwitterionic surfactant by Rossi et al. [25].

Sodium dodecylbenzenesulfonate (SDBS), a type of anion surfactant, forms spherical micelles in aqueous solutions under desirable conditions (low surfactant concentration). The spherical micelle forms a peculiar state with hydrophilic groups $(SO₃)$ distributed on the surface and nonpolar hydrophobic $((CH₂)₁₂)$ groups gathered in the interior. These electrically charged micelles selectively bind or even react with the species presented in B-Z system; hence, the micelles affect the behavior of the oscillation. Because SDBS is widely used in many fields of science and industry, we consider it relevant to investigate the effects of SDBS on a B-Z system.

Herein, we report the effects of SDBS on the $B-Z$ oscillating reaction catalyzed by a tetraazamacrocyclic Cu^H complex; the most likely mechanism that involves the formation of the SDBS micelle and the effects of the micelle on the oscillating chemical system are also discussed. This oscillating system contained a biologically active substrate (malic acid) and an enzyme-like catalyst. The findings of this work provide us with a new perspective on the connection between micelles and bio-oscillation, especially in our understanding of the steps that control the oscillatory behaviors that are influenced through the selectivity of the electrically charged micelles.

2. Experimental. – 2.1. *Reagents*. The catalyst $\lbrack \text{CuL} \rbrack (\text{ClO}_4)_2$ (*Fig. 1*) was synthesized according as described in [26] and was identified by IR spectra and by elemental analysis (anal. calc. for $C_{16}H_{32}Cl_2CuN_4O_8$: C 35.40, H 5.94, N 10.32; found: C 35.33, H 6.00, N 10.38). Other chemicals such as $Nabro₃$, H₂SO₄, and malic acid were of anal. grade and were used as received. Solns. of 0.5 m NaBrO₃. 2 м malic acid, and 1.84×10^{-2} м $\rm [CuL] (ClO_4)_2$ were prepared in 1 м $\rm H_2SO_4$. Stock solns. of 0.04 м SDBS were prepared in H₂O immediately before the experiments, and solns. with lower concentrations were freshly prepared immediately prior to use. Double dist. H_2O was used in all cases.

Fig. 1. Structure of $\vert \text{CuL} \vert \text{ClO}_4$)₂

2.2. Apparatus. The oscillating-reaction experiments were conducted in a glass container (50 ml) with a Model 79 – 3 magnetic stirrer (Jiangsu, China) and a thermostat. A Type 213 Pt electrode was used as the working electrode, and a Type 217 sat. calomel electrode, connected through a salt bridge containing $1 \text{M Na}_2\text{SO}_4$, was used as the reference electrode. The potential changes for the reactions were recorded with a model XWTD-264 y-t recorder (Shanghai, China) connected to a model PHS-25B digital voltmeter (Shanghai, China).

2.3. Procedures. Under typical oscillation conditions, the concentration of each component was as follows: $[NaBrO_3] = 1.375 \times 10^{-2}$ M, $[malic acid] = 0.2250$ M, $[[CuL](ClO_4)_2] = 3.910 \times 10^{-3}$ M, and $[H, SO_4] = 0.6475$ M. The solns. of the different components were injected into the glass container, which was maintained at $22 \pm 0.5^{\circ}$, in the following sequence: 25.9 ml of H₂SO₄ (1_M), 1.1 ml of NaBrO₃ (0.5 m) , 4.5 ml of DL-malic acid (2 m) , and 8.5 ml of $\text{[CuL]}(\text{ClO}_4)_2$ $(1.84 \times 10^{-2} \text{ m})$. We observed, under typical conditions, periodic potential changes accompanied by changes in color (orange to red to orange) of the soln. The influence of SDBS on the oscillating system was studied by injecting various amounts of SDBS into the oscillating soln. at the time when the system had completed nine potentiometric cycles and had reached the lowest point of the tenth cycle. The change in the amplitude of the oscillation, ΔA (ΔA = $A - A_0$, where A_0 and A are the amplitudes before and after the injection, resp.), and the change in the oscillation period, $\Delta T (\Delta T = T - T_0$, where T_0 and T are the periods before and after the injection, resp.), were the two parameters used to analyze the effects of SDBS on this oscillating system.

To gain more information about the mechanism of the influence of SDBS on the $B-Z$ oscillation catalyzed by the macrocyclic complex $\lbrack\text{CuL}\rbrack(\text{ClO}_4)_2$, UV/VIS spectrophotometric measurements were performed to investigate possible interactions between the SDBS micelles and $\lbrack\text{CuL}\rbrack(\text{ClO}_4)_{2}$.

3. Results and Discussion. – 3.1. The Effect of SDBS on the $|CuL|$ (ClO₄)₂-Catalyzed B-Z Oscillating Reaction. The oscillatory behavior of the system has been investigated at different temperatures. As the reaction temperature increased, the oscillation period significantly decreased, and the amplitude was also reduced, because the higher temperatures increase the speed of the reaction. Since the behavior of the oscillation was effectively influenced by the reaction temperature, the temperature of the experiment was controlled at $22 \pm 0.5^{\circ}$ to obtain a stable, typical oscillation (*Fig. 2,a*).

When the system had completed nine potentiometric cycles and reached the lowest point of the tenth cycle, different amounts of SDBS were injected into the oscillating reaction. In the presence of 1.44×10^{-4} M of SDBS, the oscillations would continue, but both the oscillation amplitude and oscillation period decreased slightly (Fig. 2,b). As the SDBS concentration increased, the oscillation amplitude and oscillation period were clearly affected. The higher the SDBS concentration, the larger the decrease in the oscillation amplitude and oscillation period (Fig. 2, c and d). The oscillation was inhibited when the concentration of SDBS was 2.4×10^{-3} M or more.

Fig. 2. The influence of different amounts of SDBS on the B-Z oscillation system. Conditions: $[NaBrO₃] = 1.375 \times 10^{-2}$ M, [malic acid] = 0.2250 M, [[CuL](ClO₄)₂] = 3.910 × 10⁻³ M, and [H₂SO₄] = 0.6475 M. a) $[\text{SDBS}] = 0$ M, b) $[\text{SDBS}] = 1.44 \times 10^{-4}$ M, c) $[\text{SDBS}] = 9.6 \times 10^{-4}$ M, and d) $[\text{SDBS}] =$ 1.92×10^{-3} м.

3.2. The Influence of the SDBS Micelles on the Oscillation Parameters. The critical micelle concentration (CMC) of SDBS in pure H_2O is 1.2×10^{-3} M; however, the CMC will be one or two orders of magnitude lower in the $B-Z$ oscillating system. The stable oscillation profile clearly changed after addition of a suitable amount of SDBS. Both the amplitude and period of the oscillation decreased. If the concentration of SDBS was greater than 2.4×10^{-5} M but lower than 2.4×10^{-3} M, the changes observed in the oscillation amplitude (ΔA) were linearly proportional to the SDBS concentration (*Fig.* 3,*a*). The following linear relationship was obtained:

$$
\Delta A = 2.94362 + 45082.79645 \times \text{[SDBS]} (R = 0.99668, N = 10)
$$

Similarly, if the concentration of SDBS was higher than 2.4×10^{-5} M but lower than 2.4×10^{-4} M, the changes observed in the oscillation period (ΔT) were linearly proportional to the SDBS concentration (*Fig. 3,b*). The following linear relationship was obtained:

$$
\Delta T = 0.07131 + 1102.28825 \times \text{[SDBS]} (R = 0.99666, N = 5)
$$

3.3. Mechanism of Action for the SDBS Micelle on the Oscillation System. Under typical conditions, the periodic potential changes, accompanied by changes in the color

Fig. 3. The linear relationship a) between ΔA and [SDBS], and b) between ΔT and [SDBS]

(orange to red to orange) of the solution, result from the changes in the concentrations of $[CuL]^{3+}$ and $[CuL]^{2+}$ $[14]$:

$$
[CuL]^{2+}(\text{red})\xrightarrow[+e^-]{-e^-} [CuL]^{3+}(\text{orange})
$$

Similar to the modified FKN model, the $[CuL]^{2+}$ -catalyzed oscillating reaction proceeds in seven steps [24] [27]. The overall reactions are as follows:

$$
BrO_3^- + Br^- + 2H^+ \rightleftharpoons HOBr + HBrO_2 \tag{1}
$$

$$
HBrO2 + Br- + H+ \rightleftharpoons HOBr
$$
 (2)

$$
HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O \tag{3}
$$

$$
BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2 BrO_2^+ + H_2O \tag{4}
$$

$$
Br_2 + HOOCHOHCH_2COOH \rightarrow Br^- + H^+ + HOOCCHOHBrCHCOOH \quad (5)
$$

$$
BrO2• + [CuL]2+ + H+ \rightarrow [CuL]3+ + HBrO2
$$
 (6)

$$
HOOCCHOHBrCHOOH + 4 [CuL]^{3+} + 3H_2O \rightarrow 4 [CuL]^{2+} + Br^- + 2 HCOOH + 2 CO_2 + 7H^+ \tag{7}
$$

Reactions $1 - 4$ are consistent with the first four reactions in classical oscillating systems catalyzed by metal ions such as Ce^{3+} or Mn²⁺. Reaction 5 is the bromination of malic acid. Reactions 6 and 7 lead to oscillations between $\lceil \text{CuL} \rceil^{2+}$ and $\lceil \text{CuL} \rceil^{3+}$ and make the color of the solution change periodically between red and orange.

As an anionic surfactant, sodium dodecylbenzenesulfonate (SDBS) aggregates to form micelles, which affect the behavior of the oscillation. There are two different types of aggregation, both of which influence the oscillation system [28]. At surfactant concentrations higher than the CMC but still low, spherical micelles can form; as the surfactant concentration increases, the spherical micelles elongate to become rod-like micelles. Because the concentration of SDBS in the $B-Z$ oscillating system is low, we assume that the micelles formed are spherical (*Fig. 4,a*). Hydrophilic groups (SO₃) are distributed on the surface of the spherical micelle, and nonpolar hydrophobic groups (hydrocarbon chains) are arranged in the interior of the sphere; some free particles $(Na⁺$ and H₂O) are inside the exterior layer of the sphere. There are various types of positively charged, negatively charged, and neutral particles in the reaction mixture. We assume that the net charge of the micelle is negative, so there are more negative charges $(SO₃)$ than positive changes $(Na⁺)$ in the micelle. The SDBS micelle can absorb some particles that are neutral or are positively charged, such as $\lceil \text{CuL} \rceil^{2+}$ and $[CuL]^{3+}$ (Fig. 4, c). When the SDBS solution was injected into the system, the micelles formed near the working electrode could absorb and bind the catalyst cations (in the form of $[CuL]^{2+}$ and $[CuL]^{3+}$).

Fig. 4. a) The structure of an SDBS micelle b) an SDBS micelle in a B-Z environment and c) catalyst ions bound to an SDBS micelle

Because the net charge of the SDBS micelles are negative, the micelles would attract more $\lceil \text{CuL}\rceil^{3+}$ than $\lceil \text{CuL}\rceil^{2+}$. This difference results in a decrease in $\lceil \text{In}(\lceil \text{CuL}\rceil^{3+} / \rceil)$ $[CuL]^{2+}$]_{max}. Therefore, a decrease was observed in the maximum potential, and this decrease led to the decrease in the oscillation amplitude. As $\lceil \text{CuL} \rceil^{3+}$ decreases, the concentration of bromide ions $(Br⁻)$ decreases according to *Reaction* 7. The decrease in the Br⁻ concentration shortens the oscillation period. As the Br⁻ concentration decreases, the concentration of $HBrO₂$ decreases in *Reaction 1*, and this decrease causes a decrease in $BrO₂$ in *Reaction 4*. As $BrO₂$ decreases, there will be a decrease in $[Cul]$ ³⁺ based on *Reaction 6*. The system returns to the oscillating state but has a shorter oscillation period and a smaller oscillation amplitude.

UV/VIS Spectral analyses were employed to verify our proposed explanation for the influence of SDBS. The maximum absorption wavelength of $\lbrack\text{CuL}\rbrack(\text{ClO}_4)_2$ was 502 nm, and at this wavelength SDBS showed no absorption; these properties facilitated measurement of the absorption of $\lbrack\text{CuL}\rbrack(\text{ClO}_4)_2$ (*Fig. 5*). The maximum absorption peak of $\lceil \text{CuL} \rceil \cdot \text{ClO}_4$)₂ did not shift upon the injection of SDBS into the $[CuL] (ClO₄)$ ₂ solution, and this lack of a shift suggests that no chemical bonds formed between the SDBS and the cationic catalyst, but that the cationic catalyst was physically bound by the micelle. The UV/VIS spectra for a constant concentration of $[CuL] (ClO₄)₂$ and different concentrations of SDBS is also shown in Fig. 5; as the concentration of SDBS increased, the absorbance of $[CuL](ClO₄)₂$ increased and the maximum absorption wavelength of $\lceil \text{CuL} \rceil \cdot \text{CO}_4$, remained at 502 nm. This phenomenon further confirmed that the negatively charged SDBS micelles bind the cationic catalyst. The CMC of SDBS in pure H_2O is 1.2×10^{-3} M, but the CMC of the ionic surfactant could significantly decrease in the presence of inorganic salt particles and a small amount of organic matter. The CMC of SDBS in this oscillating system is estimated to be 2.4×10^{-5} M. When the SDBS concentration was higher than $2.4 \times$ 10^{-5} M, the micelles formed could perturb the behavior of the oscillation by selectively attracting the catalyst cations and changing $\lceil \text{CuL}\rceil^{3+}/\lceil \text{CuL}\rceil^{2+}$. As the number of micelles in the B-Z solution increased, the SDBS micelles obviously influenced the oscillating system. Therefore, the linear decrease in the oscillation amplitude as a function of SDBS concentration can be explained. Additionally, many factors arising from the SDBS micelles, such as the surface tension, ionic strength, etc., could affect the B-Z system, and the mechanism of the action of the SDBS micelles in the oscillation may be more complicated than we had expected. Our research on these phenomena is in progress.

Fig. 5. a) UV/VIS Spectrum of 9.56×10^{-5} m SDBS. b) UV/VIS Spectra of 3.910×10^{-3} m [CuL](ClO₄)₂] with different amounts of SDBS. A, blank, $[SDBS] = 0$; B, $[SDBS] = 5.975 \times 10^{-5}$ M; C, $[SDBS] =$ 1.195×10^{-4} M; and D, [SDBS] = 1.434×10^{-4} M.

4. Conclusions. – We have shown that sodium dodecylbenzenesulfonate (SDBS) micelles formed by non-reactive aggregation can effectively influence the oscillatory behavior of a $B-Z$ system catalyzed by a tetraazamacrocyclic copper(II) complex. Both the oscillation amplitude and the oscillation period were affected by the SDBS micelles. We determined the relationship between the change in the amplitude (ΔA) and the SDBS concentration, and the relationship between the change in the oscillation period (ΔT) and the SDBS concentration. The SDBS micelles are negatively charged, and they attract more $\lceil \text{CuL} \rceil^{3+}$ than $\lceil \text{CuL} \rceil^{2+}$. The selectivity of the electrically charged micelles played a key role in controlling the oscillating reaction and resulted in changes in the oscillatory behaviors, which are reflected by a decrease of the oscillation amplitude and period. Because this oscillator includes a biologically active substrate and an enzyme-like catalyst, our findings in this work open new perspectives on the connection between micelles and bio-oscillation.

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