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Determination of Alizarin Red S using a novel B-Z oscillation system catalyzed by a tetraazamacrocyclic complex

Invited Paper

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Abstract: A new and convenient method for the determination of Alizarin Red S by the perturbations caused by different amounts of Alizarin Red S on a novel B-Z oscillating system is proposed. This new type Belousov-Zhabotinskii involves a macrocyclic copper(II) complex $[CuL](ClO_4)_2$ as catalyst and malic acid as the substrate. The ligand L in the complex is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. It is found that the relationship between the change in the oscillation amplitude and the logarithm of the Alizarin Red S concentration in the range of 1.5×10^{-7} to 1×10^{-3} M fits a polynomial model: $\Delta A = 659 + 184.2 \log$ [Alizarin Red S] $+ 12.9 \log^2$ [Alizarin Red S]. The RSD obtained with ten samples is 4.4%. The probable mechanism involving the perturbation of Alizarin Red S on the oscillating chemical system is also discussed.

Keywords: *Kinetic determination • Alizarin Red S • Tetraazamacrocyclic complex • Belousov-Zhabotinskii reaction*

1. Introduction

Oscillating chemical reactions have been widely studied in the area of theoretical and experimental chemical kinetics [1,2] over the last 50 years. Oscillating chemical reactions have also attracted great interest from scientists because of their potential application in various areas of study including chemistry, physics, mathematics, biology and life science. There are several kinds of oscillating chemical systems, such as the Belousov-Zhabotinskii oscillator, Briggs-Rauscher oscillator, Bray-Liebhafsky oscillator and the hydrogen peroxide-ferrocyanide system [3]. Among these oscillating systems, a well-known oscillating chemical reaction is the Belousov-Zhabotinskii (B-Z) reaction [4,5]. In 1958, Russian chemist Belousov first reported an oscillating reaction, the mechanism of which is oxidation of citric acid in acidic bromate medium in the presence of cerium ions. The oscillating reaction had an evident and iterative phenomenon. Then in 1964, a well-regulated oscillatory chemical phenomenon was reported by another Russian chemist Zhabotinskii. After nearly a half century, the investigations on these reactions are focused on their complex mechanisms. The famous FKN mechanism proposed by Field, Körös and Noyes [6], is of special interest and generally accepted.

The B-Z oscillating reactions have been adverted to their unusual kinetic behavior [7,8]. The first work describing a kinetic determination of a B-Z system was reported by Tichonova in 1978 [9]. Then, this method was widely used to determine many analytes. In addition, the introduction of the Analyte Pulse Perturbation technique (APP) established a milestone in the analytical investigation of the B-Z oscillation chemical reaction.

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Several subjects were determined by this technique, such as riboflavin [10], gallic acid, resorcinol [11], ascorbic acid [12], glutamic acid [13], glutathione [14], paracetamol [15], 1-naphthylamine [16], thallium [17], morphine [18], vanillin and alpha-naphthol [19].

The catalytic redox couples involved in these B-Z reaction focused on Ce^{3+}/Ce^{4+}, Mn^{2+}/Mn^{3+}, $Fe(phen)_3^{2+}/Fe(phen)_3^{3+}$ and $Ru(bpy)_3^{2+}/Ru(bpy)_3^{3+}$. Recently, macrocyclic complexes as catalyst were widely investigated. The first publication was of a catalytic macrocyclic complex of Cu(II) and Ni(II) reported by Yatimirskii in 1982 [20]. Lately, B-Z reactions catalyzed by these complexes have attracted much more attention because of their unusual oscillating features, which are reflected in lower activation energies, higher oscillating frequencies [21] and being vulnerable to external perturbations. By using macrocyclic Cu(II) or Ni(II) complexes as catalyst, the oscillating reactions involving lactic acid [22,23], malonic acid [24], and pyruvic acid [25] as organic substrate species have been studied. Recently, we have reported a new B-Z oscillating system with a tetraazamacrocyclic copper(II) complex [CuL]$(ClO_4)_2$ as catalyst and malic acid substrate [26]. The ligand, L, in the complex is 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradeca–4,11–diene . Based on this new B-Z oscillating system, Ag^+ [21] and pyrogallol [27] were determined by perturbations of analyte on the oscillating system.

Alizarin Red S is widely used as an acid–base indicator, biological colourings, metallic coloring agent, and mordant dye. It is also used for the determination of metal ions [28], generally *via* colorimetry [29]. However, direct methods for the determination of Alizarin Red S are very few. Some reported methods include spectroelectrochemistry [30], linear-sweep polarography and cyclic voltammetry [31], and electrolysis [32]. Our kinetic analytical method, which equipped with a simple instrument, provides a new method for the accurate determination of Alizarin Red S. Since Alizarin Red S contains active hydroxyls and since it has a perturbing effect on the above described new oscillating reaction, we may take advantage of these characteristics for the determination of Alizarin Red S. Experimental results show that, Alizarin Red S perturbs the new oscillating reaction by changing the oscillation amplitude. This amplitude is a polynomial function of the logarithm of Alizarin Red S concentration over the range of 1.5×10^{-7} to 1×10^{-3} M. Interferences by foreign ions were also estimated. Additionally, cyclic voltammetry (CV) and other techniques are employed to study the mechanism. A proper explanation based on the experimental results is proposed.

2. Experimental Procedures

2.1. Reagents

The tetraazamacrocyclic copper complex [CuL]$(ClO_4)_2$ was prepared according to literature [33,34], and was identified by its IR spectra and elemental analysis. All chemicals used were of analytical-reagent grade. Stock solutions of 0.6 M $NaBrO_3$, 2 M malic acid, 0.0184 M [CuL]$(ClO_4)_2$ were separately prepared in 0.9 M H_2SO_4 solution. Stock solutions of 0.001 M Alizarin Red S were prepared with double distilled water just before the experiment. Solutions with lower concentrations were made freshly just prior to use.

2.2. Apparatus

The experiments on oscillating chemical reactions were carried out in a closed system and the solutions were mixed in a glass reaction vessel (50 mL). These solutions were homogenized with a Model 79-3 magnetic stirrer (Jiangsu Jintan Guosheng Instrument Factory). A Type 213 platinum electrode (Shanghai Leici Instrument Factory) was used as the working electrode, and a Type 217 saturated calomel electrode (Shanghai weiye Instrumental plant) connected *via* a salt bridge containing 1 M Na_2SO_4 was used as reference electrode. The potentials of the electrodes *vs* time were measured with Model PHS-25B digital voltmeters (Shanghai Dapu Instrumental Factory). The kinetic curves of the reaction were recorded using a Model XWT-204 Y-t recorder (Shanghai Dahua Instrument Factory). For the measurement of cyclic voltammograms, a platinum electrode was used as working electrode, another platinum electrode as counter electrode in this reaction equipment, and a saturated calomel electrode as reference electrode.

2.3. Procedure

All of the experiments were performed at 17±0.5°C and the stirring rate was kept at 500 rpm. The platinum electrode and reference electrode were placed into the glass reaction chamber and reactants in typical condition were filled in the following sequence: 28.2 mL of 0.9 M sulfuric acid solution, 3.9 mL of 2.0 M malic acid solution, 1.2 mL of 0.6 M sodium bromate solution, and 6.7 mL of 0.0184 M [CuL]$(ClO_4)_2$ solution up to a final volume of 40 mL. The mixture was homogenized by continuous magnetic stirring and the oscillating curve was recorded by the Y-t recorder. After a short induction period, the oscillating system attained a steady state, then variable concentrations of Alizarin Red S were added into the system. Changes in the oscillation amplitude ΔA ($\Delta A = A–A_0$, where A_0 and A are the oscillation

amplitude before and after the injection, respectively) following perturbation were used as the measurement signal to construct the calibration plot.

3. Results and discussion

3.1. $[CuL](ClO_4)_2$ – Catalyzed Oscillating Reaction

For the H_2SO_4 – malic acid – $NaBrO_3$ – $[CuL](ClO_4)_2$ system, the appearance of solution color displayed periodic changes from red to orange owing to the oscillations between $[CuL]^{2+}$ and $[CuL]^{3+}$ *via* a one-electronic transfer process [26]:

$[CuL]^{2+}$ (red) $\underset{+e}{\overset{-e}{\rightleftharpoons}}$ $[CuL]^{3+}$ (orange).

The spectrum of $[CuL]^{3+}$ was accordant with the reported spectrum [35]. On the interaction with this oscillating system, Alizarin Red S caused changes both in oscillation amplitude and oscillation period but, after the perturbation, the system gradually regained the steady state.

Fig. 1 shows typical profiles for the H_2SO_4 – malic acid – $NaBrO_3$ – $[CuL](ClO_4)_2$ oscillating chemical system that obtained in the absence and presence of Alizarin Red S perturbation. During the oscillation cycle (Fig. 1a), the potential dropped gradually to a minimum (the color of the solution is red) and then increased sharply to a maximum (the color of solution is orange), where a new cycle was started. In order to ensure accurate results, several injection points have been tested throughout the oscillation cycle. The Alizarin Red S has nearly no effects on the oscillation system when injected at the maximum of the cycle, but the response was maximal when the analyte was infused at the minimum of the cycle.

The change of the trend with reaction time is shown in Fig. 1b. When the oscillation was at the steady state and after several cycles, the Alizarin Red S was injected at the minimum of the cycle. The potential dropped sharply to the minimum value and then increased to normal oscillation levels. This phenomenon is quite similar to that of the determination of hydroquinone [36] and pyrogallol [27]. The relationship between the changes of the oscillation amplitude and the logarithm of Alizarin Red S concentrations fits a polynomial relationship and the system resumes from the perturbation rapidly, so a new method could be expected to exploit this behavior for determining Alizarin Red S.

3.2 Influence of experimental variables

In order to establish the optimum working conditions for the determination of Alizarin Red S, the effects of concentrations of sodium bromate, sulfuric acid, malic acid and $[CuL](ClO_4)_2$ were studied. According to [37], the optimum value for working conditions were selected with three criteria in mind, namely: (a) maximizing the stability of the oscillating system over time, which enhances the reproducibility of the results; (b) maximizing the oscillation amplitude, which ensures maximal sensitivity for the determination of the analyte; (c) ensuring that the oscillation period allowed the effect of the analyte perturbation to be accurately determined. Accordingly, we selected ΔA and the change of the oscillation period, ΔT ($\Delta T = T - T_0$, where T and T_0 are the oscillation period before and after the injection, respectively), as the measured parameters.

Low malic acid concentrations were found to prolong the induction period, and the amplitude of the oscillation increased sharply after several short oscillation cycles

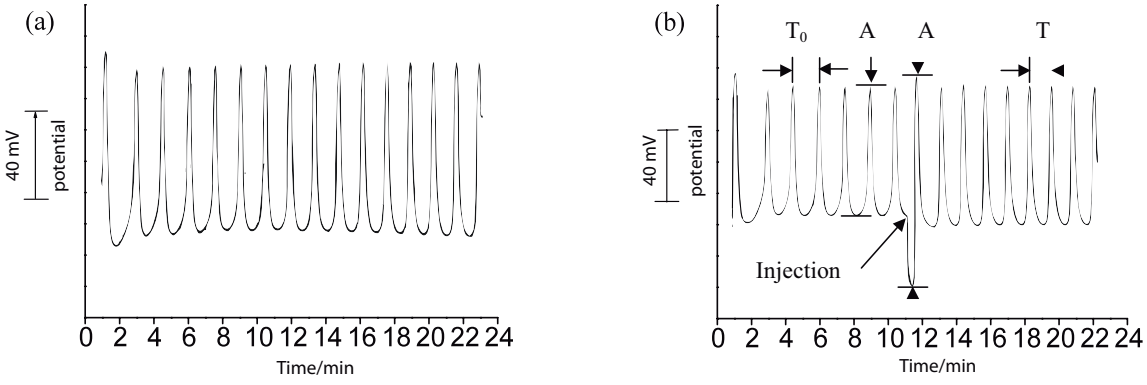


Figure 1. Typical oscillation profiles for the proposed oscillation system in the absence and presence of 5×10^{-6} M Alizarin Red S perturbation using platinum electrode. Horizontal lines mark the top and bottom of the perturbed amplitude measurement: (a) [Alizarin Red S] = 0.000 M; (b) [Alizarin Red S] = 5×10^{-6} M. Common conditions: $[NaBrO_3]$ = 0.018 M; [malic acid] = 0.195 M; $[H_2SO_4]$ = 0.9 M; $[CuL](ClO_4)_2 = 3.08\times10^{-3}$ M.

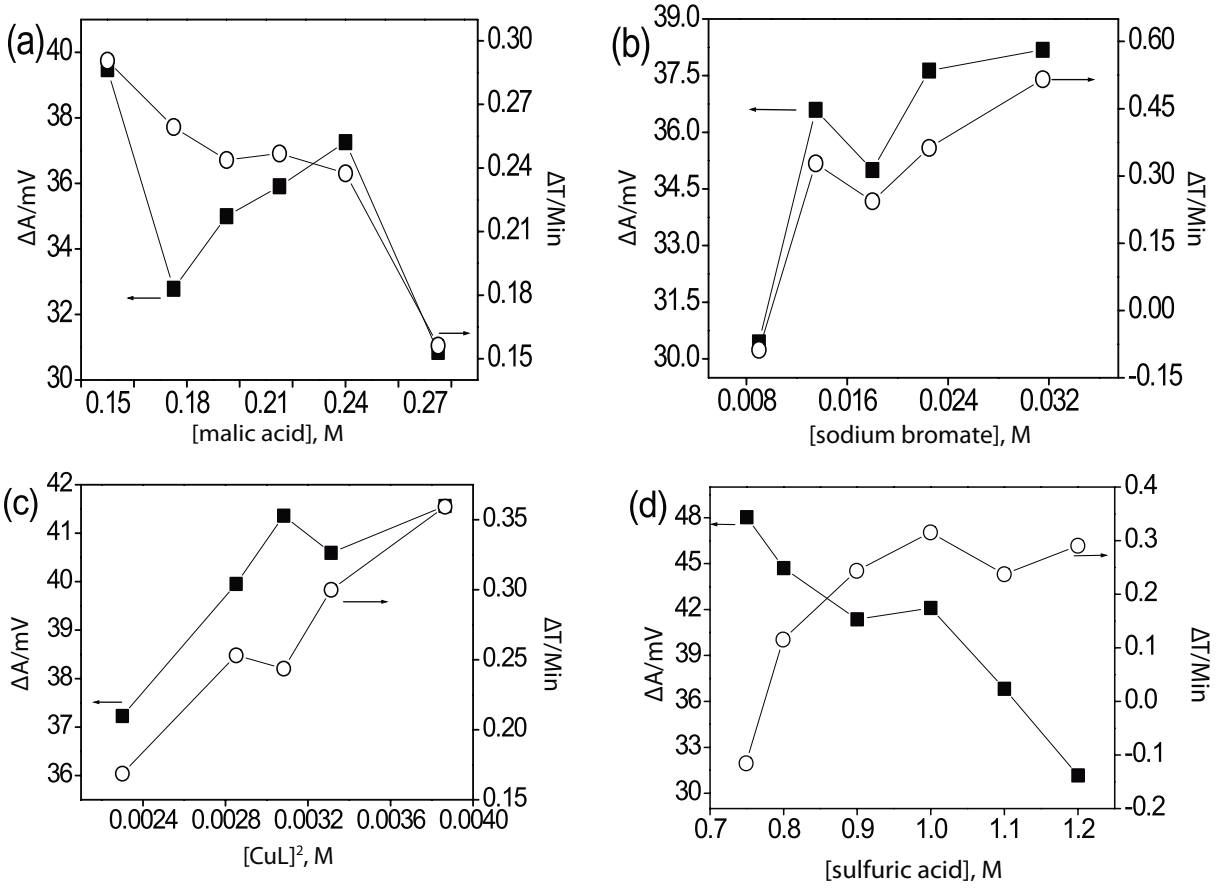


Figure 2. Influence of the concentrations of (a) malic acid; (b) Sodium bromate; (c) $[CuL](ClO_4)_2$; (d) Sulfuric acid on the Alizarin Red S perturbed oscillation system (■ refers to ΔAmplitude and ○ refers to ΔPeriod) Conditions:
(a) [$[CuL](ClO_4)_2$] = 3.08×10^{-3} M, [Sodium bromate] = 0.018 M , [Sulfuric acid] = 0.9 M, [Alizarin Red S] = 5×10^{-6} M.
(b) [$[CuL](ClO_4)_2$] = 3.08×10^{-3} M, [malic acid] = 0.195 M, [Sulfuric acid] = 0.9 M, [Alizarin Red S] = 5×10^{-6} M.
(c) [Sodium bromate] = 0.018 M , [malic acid] = 0.195 M, [Sulfuric acid] = 0.9 M, [Alizarin Red S] = 5×10^{-6} M.
(d) [$[CuL](ClO_4)_2$] = 3.08×10^{-3} M, [Sodium bromate] = 0.018 M, [malic acid] = 0.195 M, [Alizarin Red S] = 5×10^{-6} M

when the malic acid concentration is lower than 0.15 M. The influence of the malic acid was investigated over the range from 0.15 to 0.275 M. As the concentration increased, the curve of ΔA first decreased to a minimum and then reached to a maximum slowly, after that it decreased again. ΔT decreased as the malic acid concentration increased (Fig. 2a). A concentration of 0.195 M was chosen as a compromise between maximum sensitivity (oscillation amplitude) and minimum analysis time (oscillation period).

Changes in the sodium bromate concentration over the range from 0.009 to 0.0315 M had a significant effect on the behavior of the oscillation system. When the concentration of sodium bromate is lower than 0.009 M, the oscillating reaction is precarious. From Fig. 2b, it could be easily noted that with increasing sodium bromate concentration, ΔA increased to a maximum, then reached to a minimum and then increased eventually. A similar behavior in the change of the oscillation period (ΔT) was observed. A concentration of 0.018 M was chosen according to the above three criteria. Since role of sodium bromate in the mechanism of this oscillating system is explained later.

The effect of the catalyst $[CuL](ClO_4)_2$ was studied over the range from 0.0023 to 0.00386 M. The changes of period and amplitude were remarkable with increase of $[CuL](ClO_4)_2$ concentration, and the effects are illustrated in Fig. 2c. The curve of the changes in the oscillation amplitude (ΔA) increased and up to a maximum at the concentration of 0.00308 M, but it decreased subsequently with the $[CuL](ClO_4)_2$ concentration increasing. ΔT was such that it first increased and then reached a minimum, after that it increased again. A concentration of 0.00308 M was finally adopted as optimal as the system oscillated uniformly.

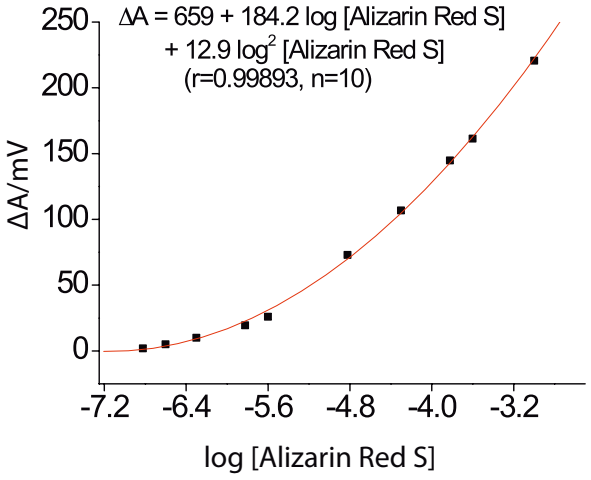


Figure 3. Calibration curve of the increase in amplitude versus the logarithm of [Alizarin Red S] in the range 1.5×10^{-7} to 1×10^{-3} M. (Common conditions: $[NaBrO_3]$ = 0.018 M; [malic acid] = 0.195 M; $[H_2SO_4]$ = 0.9 M; $[CuL](ClO_4)_2 = 3.08\times10^{-3}$ M)

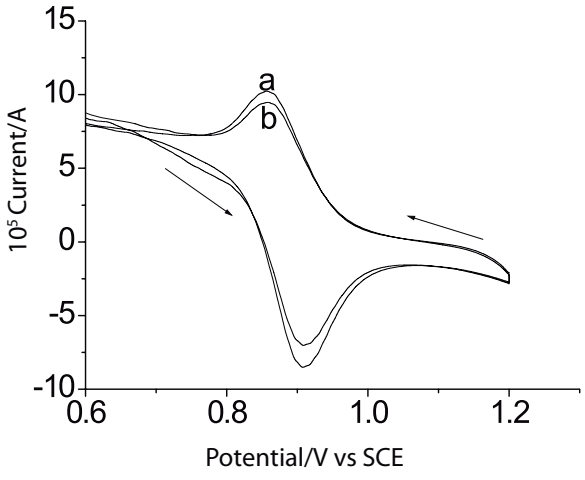


Figure 4. Cyclic voltammograms of the reactions in (a) [Sodium bromate] = 0.06 M, [Sulfuric acid] = 0.9 M, [Alizarin Red S] = 0; (b) [Sodium bromate] = 0.06 M, [Sulfuric acid] = 0.9 M; [Alizarin Red S] = 1.5×10^{-6} M; scan rate = 100 mV s^{-1}.

As the sulfuric acid concentration increase from 0.75 to 1.2 M, it resulted in a marked drift and significantly affected the amplitude and period. The increases of sulfuric acid concentration cause the decrease of the changes in oscillation amplitude (ΔA) and the increase in the changes of oscillation period (ΔT) (Fig. 2d). When the concentration of sulfuric acid is low than 0.75 M, the oscillation period become shorter and shorter, last for some short periods, and then ceased. A 0.9 M sulfuric acid concentration was finally selected as optimal since it maximizes the system response to the perturbation.

The temperature also had a strong influence on the oscillating system, which was reported in the literature by Körös *et al*. [38]. Temperature dependence and temperature compensation were reported recently [39]. Considering different purposes, the range of 10–25°C was investigated. As the system temperature increased, the oscillation period dramatically decreased whereas the oscillation amplitude increased. Increasing the temperature accelerates the reaction process and reduces the induction time. In one sense, the reduction of reaction time is useful to the analytical determination. It was indicated that the temperature has a dynamic role to command the rate of the oscillatory reaction. Nevertheless, the oscillation system response to the Alizarin Red S perturbation was not altered with the temperature change. To obtain an exact and recurrent oscillating system, the temperature was maintained at 17°C.

3.3 Approaches to the determination of Alizarin Red S

Perturbing the oscillating system by injecting variable amounts of Alizarin Red S caused a change in the oscillation amplitude and period, and the changes in oscillation amplitude were quantitatively related to the logarithm of the injected sample concentrations which were analyzed.

The perturbation experiments were achieved under the above-described optimum conditions. We used ΔA as the measured parameter. Several repeated experiments indicated that there is a polynomial relationship between ΔA and the logarithm of the Alizarin Red S concentration over the range 1.5×10^{-7} to 1×10^{-3} M (Fig. 3). The relative standard deviation (R.S.D) obtained for ten measurements of 5×10^{-6} M Alizarin Red S solution was 4.4%. The detection limit is 1×10^{-7} M.

Oscillating systems are easily altered by the presence of foreign species, so the effects of some foreign ions on the determination have been studied, as shown in Table 1. In the $[CuL]^{2+}$-catalyzed oscillating system, the amount of foreign species, causing an error of less than 5% in the determination of 5×10^{-6} M Alizarin Red S, was taken as the tolerance limit. As shown in Table 1, the selectivity of the proposed method is acceptable. The strong interference of some foreign ions, such as I^-, Cl^-, Ag^+ and Br^-, could be noted in the Table 1. Commonly, the reducing characteristic of the species and ions often had a strong effect on measurement of Alizarin Red S, which is consistent with previous results [40]:

the more reductive the species, the more interfering to the determination of the analyte.

Table1. Influence of foreign ions and species on the determination of 5×10^{-6} M Alizarin Red S.

Foreign ions and species	Tolerated ratio
Al^{3+}, Ni^{2+}, Li^{+}	10000
Na^{+}	5000
K^{+}, NH_4^{+}	2000
Mg^{2+}, Mn^{2+}, Zn^{2+}, Ac^{-}, Cu^{2+}	1000
F^{-}	100
Cl^{-}	10
Fe^{3+}, $H_2PO_4^{-}$	5
Br^{-}, Ag^{+}	0.1
I^{-}	0.01
Fe^{2+}	0.005

3.4 Mechanism of action of Alizarin Red S on the oscillating system

It is not easy to explain the interactions of the substances in the $[CuL]^{2+}$–catalyzed oscillating reaction. A few specific features, together with some common features similar to the classical one as well, are shown in the $[CuL]^{2+}$–catalyzed oscillating chemical reaction. Some radical scavengers in these oscillating systems were reported to inhibit oscillations [26]. The literature indicated that the $[CuL]^{2+}$–catalyzed system has a free radical mechanism and the concentration of bromide ion (Br^{-}) can act as an on-off switch in the oscillating reaction [6]. In analogy to the well-known FKN mechanism, a simplified mechanism is tentatively proposed for the novel oscillation [26]. The mechanism involves seven main kinetically distinct reactions and is described by reactions (1)-(7).

$$BrO_3^{-} + Br^{-} + 2H^{+} \rightleftharpoons HOBr + HBrO_2 \quad (1)$$

$$HBrO_2 + Br^{-} + H^{+} \rightleftharpoons 2HOBr \quad (2)$$

$$HOBr + Br^{-} + H^{+} \rightleftharpoons Br_2 + H_2O \quad (3)$$

$$BrO_3^{-} + HBrO_2 + H^{+} \rightleftharpoons 2BrO_2^{\cdot} + H_2O \quad (4)$$

$$Br_2 + HOOCCHOHCH_2COOH \rightarrow Br^{-} + H^{+} + HOOCCHOHBrCHCOOH \quad (5)$$

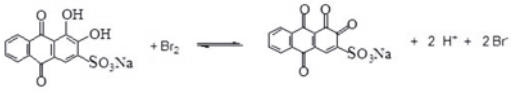
$$BrO_2^{\cdot} + [CuL]^{2+} + H^{+} \rightarrow [CuL]^{3+} + HBrO_2 \quad (6)$$

$$HOOCCHOHBrCHCOOH + 6[CuL]^{3+} + 3H_2O \rightarrow 6[CuL]^{2+} + Br^{-} + 2HCOOH + 2CO_2 + 7H^{+} \quad (7)$$

In above seven reactions, five oxidation states of bromine can be found in reactions (1)–(4). Reaction (5) represents the bromination of the malic acid and the reaction would dampen if the concentration of Br^{-} were too large. In the course of reaction (4), $BrO_2^{\cdot}$ is produced which oxidizes $[CuL]^{2+}$ in reaction (6). When $[CuL]^{3+}$ increases to a sufficient concentration, reaction (7) occurs and regenerates Br^{-}. As the concentration of Br^{-} increase, reactions (1)–(4) will continue. The reactions stop when one of the species concentrations is too low to sustain the cycle.

To clarify which species in the oscillating system reacted with Alizarin Red S, cyclic voltammetry was applied, in the absence and in the presence of Alizarin Red S, to the following media: (a) H_2SO_4 + $NaBrO_3$, (b) H_2SO_4+ $[CuL]^{2+}$, (c) H_2SO_4 + malic acid. The results indicate that only BrO_3^{-} can react with alizarin red S, as is shown in Fig. 4.

However, the direct reaction of BrO_3^{-} with species like Alizarin Red S tends to be very slow. The reaction of Br_2 with Alizarin Red S is more rapid. Therefore, it is more likely that at the first step Alizarin Red S is involved in a reaction with Br_2, which is somewhat in high concentration among the oxidation states of bromine species in the oscillation system, because malic acid does not react so quickly with Br_2 in reaction (5) as most other BZ organic substrates do. The reaction of Br_2 with Alizarin Red S gives reduction product of Br^{-} as following:



(8)

When Alizarin Red S is injected into the oscillation system, the direct reaction of Alizarin Red S with Br_2 causes a rise in Br^{-} concentration according to reaction (8) and more $HBrO_2$ is consumed in reaction (2). As the $HBrO_2$ concentration decreases, the $BrO_2^{\cdot}$ concentration will decrease accordingly because reaction (4) shifts to the left. The decrease in $BrO_2^{\cdot}$ concentration causes the decrease in $[CuL]^{3+}$ concentration in reaction (6). So the value of $\ln[CuL]^{3+}/[CuL]^{2+}$ decreases and the curve of the decrease in the potentiometric oscillation is shown in Fig. 2b.

Because the amount of Alizarin Red S added to the oscillation system was relatively low, the system resumed rapidly to an initial oscillating state after exhausting the Alizarin Red S.

Elucidating the details of the mechanism of the Alizarin Red S perturbation of this oscillating system is still problematic. However, our research may contribute to understanding the behavior of this novel oscillation system, and to the potential use of this novel oscillation system for the determination of other analytes that reduce Br_2.

4. Conclusions

The oscillation amplitude of the macrocyclic Cu(II) complex-catalyzed system increased sharply when Alizarin Red S was introduced to the system. The relationship between the changes of the oscillation amplitude and the logarithm of Alizarin Red S concentrations fits a polynomial model over the range of 1.5×10^{-7} to 1×10^{-3} M. The kinetic analytical method with a simple recording potentiometer has been established to determine Alizarin Red S. In order to establish the optimum working conditions for the determination, the effects of concentrations of sodium bromate, sulfuric acid, malic acid and $[CuL](ClO_4)_2$ were examined. A proper explanation based on the experimental results was that Alizarin Red S was oxidized by Br_2 to produce Br^-.

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