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NOTE

Determination of Xylenol Orange Based on Chemical Oscillating Reaction Catalyzed by a Macrocyclic Complex

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A new analytical method for the determination of xylenol orange based on the oscillating system is proposed. The oscillating system involves a macrocyclic complex $[CuL](ClO_4)_2$ as catalyst, malic acid as organic substrate and sodium bromate as oxidant. The ligand L in the complex is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The experimental results show that, when the system is perturbed by adding variable amounts of xylenol orange, the change of the oscillation amplitude is linearly proportional to the concentration of logarithm of the xylenol orange in the range 2.5×10^{-7}-2.5×10^{-4} M. Hence, an array of xylenol orange involving its perturbation effects on a Belousov-Zhabotinsky system has been established.

Key Words: Chemical oscillating reaction, Xylenol orange, Determination, Macrocyclic complex.

Chemical oscillating reaction, which exhibits periodic changes in concentration of some species (usually a reaction intermediate), occurs only in the non-equilibrium systems[1]. A Belousov-Zhabotinsky (BZ) reaction reaction, one of the most famous examples of chemical oscillations, has been studied owing to its unique kinetic non-equilibrium features[2-4]. These kinetic features have made such system potentially useful in the analytical chemistry field and some methods for determinations of analytes based on their perturbation effects on Belousov-Zhabotinsky reaction have been reported. These analytes include Ag^+ ion[5], $[Fe(CN)_6]^{3-}$ or $[Fe(CN)_6]^{4-}$ ion[6], hydroquinone[7] and vitamin C[8].

Oscillating reactions catalyzed by macrocyclic complex of Cu(II) or Ni(II) were first discovered by Yatisimirskii and Tikhonova[9]. Recently, we have reported series of macrocyclic complex-catalyzed oscillating systems[10-13]. We have studied unique features of a macrocyclic complex-catalyzed oscillating system[10]: $NaBrO_3$-H_2SO_4-malic acid-$[CuL](ClO_4)_2$, where the ligand L in the complex $[CuL](ClO_4)_2$ is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. We have also used this $[CuL](ClO_4)^{2-}$ catalyzed oscillating system for kinetic determination of Ag^+ [14], pyrogallol[15], calcium pantothenate[16], Alizarin red S[17] and catechol[18]. In this notes, we have surveyed the effect of xylenol orange perturbation on this novel Belousov-Zhabotinsky system.

The catalyst $[CuL](ClO_4)_2$ was prepared according to literature methods[14,19,20] and was identified by IR spectra and elemental analysis. All chemicals used were of analytical reagent grade. Solutions of 0.6 M $NaBrO_3$, 2 M malic acid, 0.0221 M $[CuL](ClO_4)_2$ were prepared in 1.15 M sulfuric acid. Solutions of 0.01 M xylenol orange were made immediately before the experiment. Solutions with lower concentrations were prepared prior to use. Double distilled water was used in all cases.

The oscillating reaction experiments were conducted by the methods as described previously[15,18]. The perturbation experiments were carried out by injecting 0.2 mL of sample containing variable amounts of xylenol orange to oscillating system in steady state, causing the amplitude to increase sharply. Thus, changes of oscillating amplitude $\Delta A = A - A_0$ (A_0 and A are the oscillation amplitude before and after the injection, respectively) were used as parameter to determine xylenol orange (Fig. 1).

We performed perturbation experiments under the following conditions: $[NaBrO_3] = 0.015$ M; [malic acid] = 0.2 M; $[H_2SO_4] = 1.15$ M; $[CuL](ClO_4)_2 = 2.65 \times 10^{-3}$ M. The response to the xylenol orange perturbation was obtained by employing changes in oscillation amplitude (ΔA) *versus* different concentrations of xylenol orange. The change in oscillation amplitude (ΔA) obtained is linearly proportional

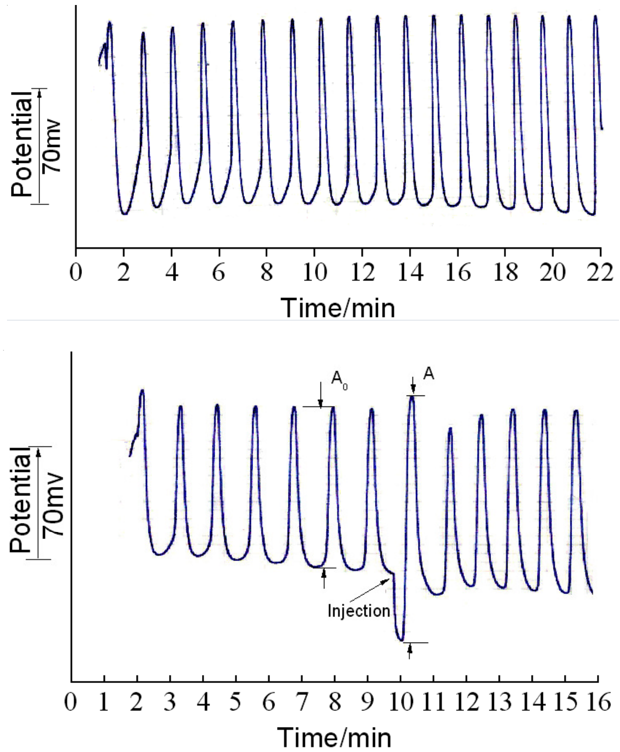

Fig. 1. Typical oscillation profiles for the proposed oscillation system in the absence and presence of variable amounts of xylenol orange perturbation using platinum electrode: (a) [Xylenol orange] = 0.000 M, (b) [xylenol orange] = 5.0×10^{-5} M. Common conditions: $[NaBrO_3]$ = 0.015 M; [malic acid] = 0.2 M; $[H_2SO_4]$ = 1.15 M; $[CuL](ClO_4)_2 = 2.65 \times 10^{-3}$ M

to the logarithm of the xylenol orange concentration over the range of 2.5×10^{-7}-2.5×10^{-4} M (Fig. 2). The calibration data obtained obey the following linear regression equation:

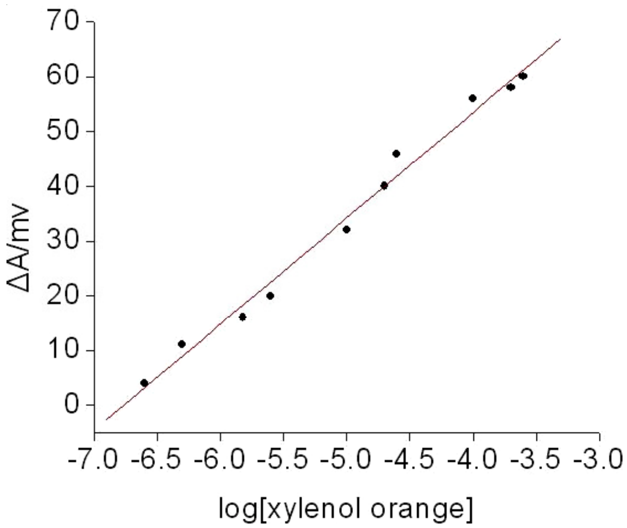

Fig. 2. Calibration curve of the increase in amplitude *versus* the logarithm of [xylenol orange] in the range of 2.5×10^{-7}-2.5×10^{-4} M. Common conditions: $[NaBrO_3]$ = 0.015 M; [malic acid] = 0.2 M; $[H_2SO_4]$ = 1.15 M; $[CuL](ClO_4)_2 = 2.65 \times 10^{-3}$ M

$$\Delta A = 130.96 + 19.34 \log [\text{xylenol orange}]$$
$$(R = 0.99388, N = 10)$$

The precision (RSD), calculated from five perturbations of 5.0×10^{-5} M xylenol orange, was 4.3 %. The detection limit obtained is 1.3×10^{-7} M. Such a precision is quite acceptable.

Table-1 shows the effects of some foreign species on the determination. It is found that Ag^+, Cl^-, Mn^{2+}, I^- and NO_2 have serious interference. Ca^{2+}, Mg^{2+}, Al^{3+}, Ni^{2+} and Li^+ show no interference on determination. The results are acceptably selective.

TABLE-1
EFFECTS OF THE SOME FOREIGN SPECIES

Foreign ions and species	Tolerated ratio
Ca^{2+}, Mg^{2+}, Al^{3+}	1300
Ni^{2+}, Li^+	100
Fe^{3+}, Zn^{2+}	10
Glucose, phenol, F^-, OAc^-, Cu^{2+}	1
Ag^+	0.5
Cl^-	0.1
Mn^{2+}	0.05
I^-, NO_2^-	0.01

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