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Determination of eugenol by using a Briggs - Rauscher system catalyzed by a macrocyclic nickel (II) complex

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ABSTRACT

This paper reports a new method for determination of tracing amounts of eugenol (EUG) by its perturbation effects on a novel Briggs–Rauscher (BR) oscillating system catalyzed by a macrocyclic complex $[NiL](ClO_4)_2$. The ligand L in the complex is 5, 7, 7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. In this novel BR oscillator, not only a macrocyclic complex was used as a catalyst to replace Mn^{2+}, but the value of pH in the system was kept at pH of stomach fluids (pH ≈2.0) as well. Experimental results have shown that addition of EUG into the BR system could quench and then successively regenerate the oscillations, accompanying by an inhibitory time that relies on the concentration of the EUG added. An assay was thus established by employing such a BR system for determining EUG. The relationship between inhibition time and EUG concentrations is obtained over the range between 5.00×10^{-7}–2.50×10^{-5} M. Two calibration curves are thus achieved: linear regression over the range 5.00×10^{-7} to 1.25×10^{-5} M of EUG, and polynomial regression over the range $1.25 \times 10^{-5} \sim 2.50 \times 10^{-5}$ M of EUG. The obtained RSD from seven measurements of 1.00×10^{-5} M of EUG is 3.75%, and from 1.50×10^{-5} M of EUG is 2.05%. Some factors influencing the determination were also examined. Not only has the method been successfully applied to determine EUG but it could be extended to determine other lipophilic antioxidants as well. Furthermore, the possible reaction mechanism using the FCA model has been proposed.

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1. Introduction

Oscillatory chemical system, which occurs at far-from equilibrium and which was controlled by complex dynamics, has already been used as a matrix to analyze the organic compounds and inorganic ions. Among all oscillating systems, both Belousov–Zhabotinskii (BZ) type of reaction (with Ce^{4+}, Mn^{2+}, $Fe(phen)_3{}^{2+}$, or $Ru(bipy)_3{}^{2+}$ as catalysts [1–4]) and Briggs–Rauscher (BR) type of reaction involving metal ion catalysts (Ce^{4+}, Mn^{2+}) [5,6] have been extensively studied. Recently, the macrocyclic nickel and copper complexes have been discovered to catalyze BR [7,8] or BZ [9] oscillatory reactions as alternative catalysts. Compared with other one-electron-transfer metal ion catalysts (like Mn(II) or Ce(IV)), macrocyclic complexes, however, possess the extended π-system in the macrocyclic ligands which ensure a high rate for reactions involving electron transfer at individual steps of the oscillating process [10]. Our previous work indicated that macrocyclic copper complexes could catalyze BZ oscillators [11–13] and such oscillators could be utilized in detection of some species and ions [10,14–17] as well.

As a new analytical method, coupling Mn^{2+}-catalyzed BR reaction [5] with the measurement of antioxidative activity has been reported recently [18–20] [21,22]. Such BR system involves of the iodination and oxidation of an organic substrate (malonic acid (MA) or its derivatives) by acidic iodate in the presence of H_2O_2 with the Mn^{2+} ion as a catalyst [23]. When antioxidants were added to an active oscillating BR mixture involving free radical intermediates, they would react with such free radical intermediates, resulting in quenching and subsequently regenerating oscillations. The inhibitory effect of antioxidants relies on the concentration of the antioxidant added in a wide range of concentration; a method for assay of antioxidant was thus established.

Until now, the application of classical Mn^{2+}-catalyzed BR reaction for measurement of aqueous-soluble (hydrophilic) antioxidants has been described, but such reaction has rarely been used for measurement of lipophilic antioxidants. Cervellati etc [18] dealt with the inhibitory effects caused by antioxidants on the Mn^{2+}-catalyzed BR-system in mixed 20% EtOH-H_2O medium; they found that the numbers of oscillations as well as the oscillatory time (i.e.

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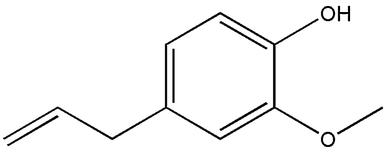

Fig. 1. Structure of eugenol (EUG).

the duration of the oscillatory regime) are much smaller in the mixed medium than in aqueous solution.

In an effort to expand the BR family fitting for measurements of lipophilic antioxidants, we survey a BR system catalyzed by a macrocyclic nickel complex [NiL](ClO_4)$_2$, where L in the ligand is is 5, 7, 7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. We demonstrated that, for the first time, a macrocyclic complex - catalyzed BR oscillator is completely appropriate for lipophilic antioxidant eugenol (EUG) assays. This analytical work for determination of such antioxidant was performed near the pH of stomach fluids (pH ≈2.0). Generally, some antioxidants exist naturally in some plants and even in some healthy foods. And antioxidants in foods, after enter the mouth, could show their antioxidant activity capacity against free radicals generated in the stomach, where foods are broken-down in human digestion process. Therefore, such a BR method provides meaningful information on determination some antioxidants as well as the antioxidant activity at the pH of stomach fluids.

Eugenol (EUG), a phenylpropene, is a lipophilic antioxidant. Its IUPAC name is 4-Allyl-2-methoxyphenol. It is a pale yellow oily liquid extracted from clove oil, nutmeg or bay leaf. It was commonly used in the field of cosmetic, medicine [24], dentistry, chemical industry and food [25] as antiseptic, anesthetic, intermedium, stabilizers and antioxidants. Usually, it is also harmful to the liver [26] and possible overdose could cause an adverse reaction such as convulsions, diarrhea, dizziness, or rapid heartbeat [27]. Thereby, a novel method for the measurement of EUG is required. The structure of EUG is shown in Fig. 1.

Some methods for the determination of EUG have been reported, such as HPLC-UV [28], gas chromatography/mass spectrometry [29], Δε-method [30]. Compared to instrumental analysis, the oscillating chemical reaction as an analytical tool has some advantages such as simple in set-up, easy for the operation, largely linear range and the lower detection limit. Our quantitative analytical method, with a simple instrument, provides a new method for precise determination of EUG, which can be detected in the range of $5.00 \times 10^{-7} \sim 2.50 \times 10^{-5}$ M.

2. Experimental

2.1. Apparatus

Oscillating experiments were run in a glass vessel and the temperature was kept at 4.0 ± 0.5 °C by using a thermostat (DZCS-IIC, Nanjing DazhanKejiao Institute of Instrument, China). A Model 79-3 magnetic stirrer (Jiangsu, China) was utilized to homogenize the solutions. A Type 213 platinum electrode (Shanghai, China) and a Model 217 saturated calomel electrode (SCE) (Shanghai, China) connected via a salt bridge containing 1 M Na_2SO_4 as reference electrode were used to follow the changes of potential. These two electrodes were finally controlled by a personal computer (PC); an *amplifier* (Vernier Software Technology, USA) and a *Go!Link* sensor interface (Vernier Software Technology, USA) were introduced between the electrodes and PC. The value of pH was measured by a *pH sensor* (Vernier Software Technology, USA) connected to the other *Go!Link* sensor interface (Vernier Software Technology, USA); this interface was also controlled by the same PC described above. The *Logger Lite* data-acquisition programme was utilized.

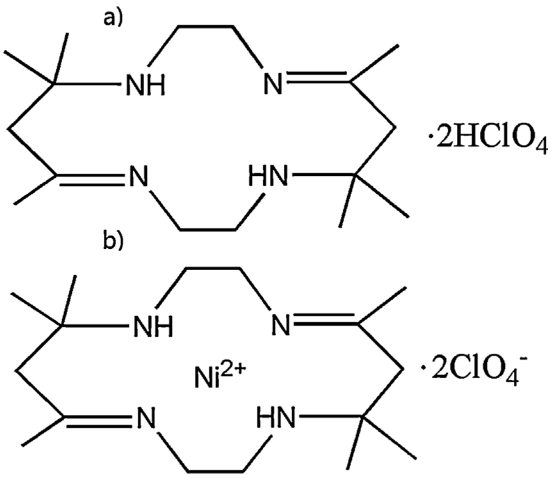

Fig. 2. (a) The structure of perchlorate ligand (L ·2HClO$_4$); (b) the structure of [NiL](ClO_4)$_2$.

For the measurement of cyclic voltammetry: a Type 213 platinum electrode was used as the working electrode, a saturated calomel electrode (SCE) as reference, and a platinum wire as the counter electrode.

2.2. Reagents and procedure

Malonic acid, KIO_3, H_2O_2 (30%), EUG and H_2SO_4 (Aldrich, 98%) were purchased commercially. All reagents were analytical reagent grade unless noted. Double distilled water was used in all cases. Solutions of H_2O_2 were made from 30% aqueous material without stabilizer. 2.50×10^{-2} M H_2SO_4 was diluted from 98% H_2SO_4, and the following initial concentrations of reactants were prepared in 2.50×10^{-2} M H_2SO_4: 1.40×10^{-1} M KIO_3, 2.00 M malonic acid, 1.73×10^{-2} M [NiL](ClO_4)$_2$, and 4.00 M H_2O_2. Solutions of 5.00×10^{-2} M EUG were dissolved in absolute ethyl alcohol. Solutions with lower concentrations of EUG were prepared prior to use. The experiments were carried out in an ice-water bath environment in a thermostat to keep the temperature at 4.0 ± 0.5 °C.

2.2.1. Synthesis of the perchlorate ligand (L ·2HClO$_4$) (Fig. 2a)

The perchlorate ligand (L ·2HClO$_4$) was according to Ref. [31]. 63.0 mL perchloric acid (70%) was dropwisely added into a 500.0 mL round bottom flask containing 49.2 mL ethylene-diamine under vigorous stirring at 0.0 °C. After the solution becoming transparent, a stock of anhydrous acetone (112.0 mL) was added and vigorous stirring was kept for 2 ~ 4 h. The white precipitate, which was crystallized from the solution, was filtered and washed with acetone and ethanol. The bright white crystals were obtained by recrystallization from hot methanol. The structure of the perchlorate ligand (L ·2HClO$_4$) is shown in the Fig. 2 (a). (Elemental analysis for $C_{16}H_{34}N_4Cl_2O_8$ Theoretical: C, 39.92; H, 7.07; N, 11.64%. Found: C, 40.11; H, 7.10; N, 11.49%.)

2.2.2. Synthesis of tetraazamacrocyclic nickel complex [NiL](ClO_4)$_2$ (Fig. 2b)

Tetraazamacrocyclic nickel complex [NiL](ClO_4)$_2$ was prepared according to literature [32]. In a 1000.0 mL round-bottom flask, 500.0 mL methanol, 24.9 g Ni $(Ac)_2{\cdot}4H_2O$ (0.1 mol) and 48.1 g perchlorate ligand (L ·2HClO$_4$) (0.1 mol) were mixed together. The mixture was stirred under reflux for 4 h until yellow precipitate began to form. Then, the solution was filtered and concentrated to one third its original volume. After 24 hours, the yellow crystal,

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