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Resonance Rayleigh scattering, second-order scattering and frequency doubling scattering spectra for studying the interaction of erythrosine with $Fe(phen)_3^{2+}$ and its analytical application

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ABSTRACT

In a weak alkaline Britton–Robinson buffer medium, erythrosine (Ery) can react with $Fe(phen)_3^{2+}$ to form 1:1 ion–association complex, which will cause not only the changes of the absorption spectra, but also the remarkable enhancement of resonance Rayleigh scattering (RRS), second-order scattering (SOS) and frequency doubling scattering (FDS) spectra, and the appearance of new spectra of RRS, SOS and FDS. The maximum RRS, SOS and FDS wavelengths ($\lambda_{ex}/\lambda_{em}$) of the ion–association complex are located at 358/358 nm, 290/580 nm and 780/390 nm, respectively. The increments of scattering intensities (ΔI) are directly proportional to the concentration of Ery in a certain range. The detection limits for Ery are 0.028 $\mu g\,mL^{-1}$ for RRS method, 0.068 $\mu g\,mL^{-1}$ for SOS method and 0.11 $\mu g\,mL^{-1}$ for FDS method, respectively. Among them, the RRS method has the highest sensitivity. Based on the above researches, a new highly sensitive and simple method for the determination of Ery has been developed. In this work, the spectral characteristics of absorption, RRS, SOS and FDS spectra, the optimum conditions of the reaction and influencing factors for the RRS, SOS and FDS intensities were investigated. In addition, the reaction mechanism was discussed.

1. Introduction

Advances in the food industry in the past century have allowed many dairy products to be made with a variety of flavors and colors in order to enhance their taste and visual aesthetics, and to promote sales.

Unfortunately, many of the natural colorants do not have the same stability under processing conditions as the synthetic ones. However, some of these substances pose a potential risk to human health, especially if they are excessively consumed. For this reason, safety data, such as the acceptable daily intake, based on toxicological studies on experimental animals and human clinical studies, have been repeatedly determined and evaluated by Food and Agricultural Organization (FAO) and World Health Organization (WHO) [1].

Although the number of permitted food colorants was reduced for food safety reasons in recent years, many kinds of synthetic food dyes are still widely used all over the world because of their low price, effectiveness and stability. In China, erythrosine (Ery, E-127) as a kind of colorant is used as a food additives at a maximum limit of 0.05 g/kg of the product [2]. Facing with increasing legal restrictions, food colorant determination became an analytical challenge. Consequently, accurate and reliable methods for the determination of synthetic colorants are required for the assurance of food safety.

The present national standard methods for the determination of food colorant are high-performance liquid chromatography with gradient elution, thin layer chromatography, and oscillopolarography in China [3]. In addition, a large number of analytical methods for food color erythrosine have been proposed, such as ion-pair reversed-phase high-performance liquid chromatography (IP–RP–HPLC) [4], capillary electrophoresis (CE) [5,6], capillary electrophoresis with laser-induced fluorescence detection (CE–LIF) [7], chemiluminescence (CL) [8] and spectrophotometry (SP) [9]. HPLC possesses high sensitivity but it also needs complex pre-treatment and takes a long time to separate. Capillary electrophoresis gives high resolution and short analysis time, but has sensitivity problem as a result of small injection volume and tailing. Chemiluminescence and spectrophotometry are simple and rapid methods, however, their sensitivities are low and only suitable for the determination of erythrosine in samples with simple components. Consequently, it is necessary for developing other new methods which are simple, fast and highly sensitive for the determination of food color erythrosine.

The new analytical techniques of resonance Rayleigh scattering (RRS), second-order scattering (SOS) and frequency doubling scattering (FDS) have been given much attention because of their

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high sensitivity, simplicity and rapidness, and have been studied more and more. They have been applied to the study and determination of macromolecules such as nucleic acids [10,11], proteins [12–14], polysaccharides [15–21], surfactants [22,23], inorganic ions [24–28], pharmaceuticals [29–41], lysozyme [42], and triphenylmethane dyes [43]. In particular, with the rapid development of nanotechnology, great attention has been focused on the use of nanoparticles and quantum dots (QDs) as the RRS probes, such as Au nanoparticles [44–49], Ag nanoparticles [50], core-shell of Au–Ag nanoparticles [51] and QDs [52,53]. In addition, it has been applied to the determination of β-cyclodextrin inclusion constant [54,55] and the critical micelle concentration of surfactant [56]. However, to our best knowledge, there is no report about the investigation of RRS, SOS and FDS spectra for the determination of food colorant Ery.

In this paper, we studied the interaction between Ery and $Fe(phen)_3^{2+}$. $Fe(phen)_3^{2+}$ was adopted as the RRS, SOS and FDS probe for the determination of food color Ery in a certain range. The probe showed the high sensitivity and good stability for the determination of Ery. The interaction mechanism of the system was also studied combined with the transmission electronic microscopy (TEM) and UV-Vis spectrometry.

2. Materials and methods

2.1. Reagents

Erythrosine (Ery) standard solution was prepared by dissolving 0.0200 g of Ery (National Institute for the Control of Pharmaceutical and Biological Products, Beijing, China) in doubly distilled water, and diluting to the mark in a 100 mL brown calibrated flask for stock solution. The working solution was further diluted with water to 20 μg mL^{-1}. A 1.0×10^{-2} mol L^{-1} stock solution of $Fe(phen)_3^{2+}$ was prepared by dissolving 0.2780 g of $FeSO_4 \cdot 7H_2O$ in 10 mL of concentrated H_2SO_4, to which 0.5950 g of phenanthroline and a few ascorbic acid had been added, and then diluting to the mark in a 100 mL brown volumetric flask. The working solution of 1.0×10^{-4} mol L^{-1} $Fe(phen)_3^{2+}$ was obtained by diluting the stock solution with water.

Britton–Robinson (BR) buffer solutions (pH 1.8–12.0) were prepared by mixing 0.2 mol L^{-1} NaOH and mixture of 0.04 mol L^{-1} H_3PO_4, H_3BO_3 and CH_3COOH according to suitable proportion and pH values were adjusted using a pH meter. HAc–NaAc buffer solutions (pH 1.6–7.5) were prepared by mixing 0.2 mol L^{-1} HAc and 0.2 mol L^{-1} NaAc solutions according to certain proportion. HCl–NaAc buffer solutions (pH 0.65–5.5) were prepared by mixing 1.0 mol L^{-1} HCl and 1.0 mol L^{-1} NaAc solution. The pH values of solutions were adjusted by a pH meter. All solutions were prepared with doubly distilled water and all chemicals were of analytical reagent grade, unless otherwise stated.

2.2. Apparatus

A Hitachi F-4500 spectrofluorophotometer (Tokyo, Japan), which was equipped with a 150-W xenon lamp, was used for recording the RRS, SOS and FDS spectra and for measuring the scattering intensities at a given wavelength with the slits (E_x/E_m) of 10.0/10.0 nm and the PMT voltage of 400 V. A UV–vis 8500 spectrophotometer (Tianmei, Shanghai, China) was used for recording the absorption spectra and measuring absorbance. A pHs-3C pH (Dazhong Analytical Instrumental Plant, Shanghai, China) was used to adjust solution pH. HITACHI-600 transmission electron microscopy (TEM, Electronic Company of Japan) was used to observe the appearance and size of nanoparticles, the accelerating voltage of which is 400 V.

Table 1
RRS spectral characteristics.

System	λ_{max} (nm)	λ_{other} (nm)
Ery	358	545
$Fe(phen)_3^{2+}$	348	
$Fe(phen)_3^{2+}$–Ery	358	595

2.3. General procedure

A 1.0 mL of 1.0×10^{-4} mol L^{-1} $Fe(phen)_3^{2+}$ solution was pipetted into a 10 mL calibrated flask followed by appropriate amounts of the erythrosine working solution and 1.0 mL of pH 8.0 BR buffer solution. The solution was diluted to the mark with doubly distilled water and mixed thoroughly. After 10 min, the RRS spectra of the system were recorded with synchronous scanning at $\lambda_{em} = \lambda_{ex}$, and the SOS and FDS were recorded at $\lambda_{em} = 2\lambda_{ex}$ and $\lambda_{em} = 1/2\lambda_{ex}$, respectively. The I_{SOS} and I_{FDS} were plotted versus the different wavelengths to obtain SOS and FDS spectra. Then, the scattering intensities, I_{RRS}, I_{SOS} and I_{FDS}, for the reaction product, and I^0_{RRS}, I^0_{FDS} and I^0_{SOS} for the reagent blank at their own maximum scattering wavelengths, $\Delta I_{RRS} = I_{RRS} - I^0_{RRS}$, $\Delta I_{SOS} = I_{SOS} - I^0_{SOS}$ and $\Delta I_{FDS} = I_{FDS} - I^0_{FDS}$, were measured. Simultaneously, the absorption spectra were recorded.

3. Results and discussion

3.1. Spectral characteristics

3.1.1. RRS spectra

The RRS spectra of Ery–$Fe(phen)_3^{2+}$ system are shown in Fig. 1. The RRS spectral characteristics of the system are listed in Table 1. It can be seen from Fig. 1 and Table 1 that: (1) the RRS intensities of Ery and $Fe(phen)_3^{2+}$ themselves are very weak; however, when they react with each other to form the ion–association complexes of Ery–$Fe(phen)_3^{2+}$, strong RRS signal and a new RRS spectrum can be observed. The maximum RRS peak is located at 358 nm; (2) the RRS peaks of the ion–association complexes of Ery–$Fe(phen)_3^{2+}$ are located at 358 nm and 595 nm, whereas the scattering peaks of Ery are located at 358 nm and 545 nm, illustrating that the new scattering peak appearing at 595 nm of the Ery–$Fe(phen)_3^{2+}$ complexes is the characteristic peak and has a red shift of 50 nm compared with that of Ery; (3) the RRS intensity (ΔI_{RRS}) is directly proportional to the concentrations of Ery (Fig. 1b). Based on this phenomenon, a highly sensitive method for the determination of Ery has been developed.

3.1.2. SOS and FDS spectra

The spectra of SOS and FDS for the Ery–$Fe(phen)_3^{2+}$ system were investigated, respectively, and the results showed that the intensities of SOS and FDS for Ery and $Fe(phen)_3^{2+}$ themselves are very weak. However, when they interacted to form ion–association complexes, the SOS and FDS intensities are enhanced obviously. The maximum scattering wavelengths (λ_{ex}/λ_{em}) appear at 290 nm/580 nm for the SOS spectrum and 780 nm/390 nm for the FDS spectrum. In addition, there is also another smaller peak for SOS at 240 nm/480 nm. We chose 290 nm/580 nm for SOS and 780 nm/390 nm for FDS as the detection wavelengths because of the high signal-to-noise. In this condition, the enhancement of two kinds of scattering intensities (ΔI_{SOS} and ΔI_{FDS}) for Ery is linear with an increase in concentration of Ery in a certain range. Therefore, the SOS and FDS method can be applied to the determination of Ery.