

Complexation equilibrium between iron(III) and *N,N'*-bis(2-hydroxyphenylmethyl)-*N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine

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Abstract. Complexation equilibrium between iron(III) and *N,N'*-bis(2-hydroxyphenylmethyl)-*N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine (H_2bbpen), a colorless hydrophobic divalent hexadentate ligand, and potential use of the ligand for the spectrophotometric determination of iron(III) in aqueous solution was investigated. In the pH range 2.0 – 3.0, Fe(III) forms stable 1:1 complex with H_2bbpen , and Fe(III) can be determined selectively as the purple $Fe(bbpen)^+$ complex ($\lambda_{max} = 560$ nm, $\epsilon = 4.3 \times 10^3$ dm³ mol⁻¹ cm⁻¹, $\log \beta_1 = 32.6 \pm 0.1$). In this system, linear calibration range of Fe(III) was $5 \times 10^{-6} - 2 \times 10^{-4}$ mol dm⁻³ ($0.3 - 12$ μ g cm⁻³) and detection limit was 3×10^{-6} mol dm⁻³ (0.2 μ g cm⁻³). Furthermore, most of foreign metal cations did not influence largely the determination of Fe(III).

Key words. *N,N'*-bis(2-hydroxyphenylmethyl)-*N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine – iron(III) – complexation – spectrophotometric determination.

Introduction

As well known, iron(III) forms colored complexes with many of phenol derivatives. On the basis of this nature, a lot of phenolic compounds have been developed as reagents for the spectrophotometric determination of Fe(III) [1]. However, most of them have several disadvantages: the reagents themselves often have absorption band in visible region because of their conjugation structures, and they often form colored complexes with not only Fe(III) but also other several metal cations.

Recently, Davis et al. [2] reported that catechol derivatives-Fe(III)-polyamines ternary complexes have far stronger absorption bands than respective catechol derivatives-Fe(III) binary complexes. This report suggests potential development of a phenolic polydentate ligand having nitrogen donors as a novel reagent for the determination of Fe(III).

The compound *N,N'*-bis(2-hydroxyphenylmethyl)-*N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine (H_2bbpen) [3,4] is a colorless hydrophobic divalent hexadentate ligand having two phenolate-oxygen, two amine-nitrogen and two pyridine-nitrogen donor atoms. Several researchers investigated complexation [3-9] and protonation [9,10] property of H_2bbpen or its analogues. In this study, we investigated complexation equilibrium between Fe(III) and H_2bbpen in aqueous solution. Furthermore, potential use of H_2bbpen as reagent for the spectrophotometric determination of Fe(III) was studied.

Experimental

Reagents and apparatus

The synthesis of H_2bbpen was performed according to the methods of Neves et al. [4] All other chemicals were reagent-grade materials and distilled deionized water was used throughout.

The absorption spectra of solutions at 20 ± 1 °C were recorded on a JASCO U-best 30 or a Shimadzu UV-160 UV-visible spectrophotometer in the range of 400 – 800 nm using 1 cm matched quartz cells. The pH values were obtained using a Hitachi-Horiba F-12 pH meter with a Horiba 6366-10D combined glass electrode.

Standard procedure

Into an aliquot of sample solution containing Fe(III), 1 cm³ of 3×10^{-2} mol dm⁻³ H_2bbpen - 0.1 mol dm⁻³ nitric acid was added, after which the solution was diluted to 10 cm³ with 0.1 mol dm⁻³ sodium hydroxide and water and the pH was adjusted to 2.3. After leaving the solution for 2 h or immersing it in a water bath at 50 °C for 10 min, the absorbance was measured at 560 nm against pure water.

Results and discussion

Identification of Fe(III)- H_2bbpen complex

Figure 1 shows visible absorption spectrum of aqueous solution (pH 2.3) containing equimolar of Fe(III) and H_2bbpen .

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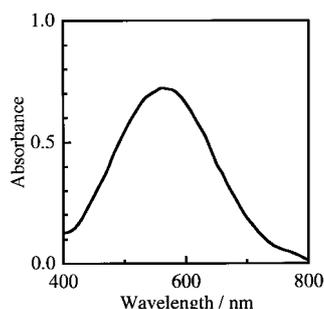


Fig. 1. Visible absorption spectrum of aqueous solution (pH 2.3) containing 1.67×10^{-3} mol dm^{-3} of Fe(III) and 1.67×10^{-4} mol dm^{-3} of H_2bbpen .

Although neither individual solution of Fe(III) nor that of H_2bbpen has absorption in the range of 400 – 800 nm, the mixture was purple and had absorption maximum at 560 nm, showing the formation of Fe(III)- H_2bbpen complex. The absorbance of the Fe(III)- H_2bbpen solution was maximum and constant in the pH range 2.0 – 3.0. The decrease of the absorbance in lower pH seems to be originated from the protonation of H_2bbpen [9,10], and the slight decrease in higher pH may be caused by the hydrolysis of Fe(III) [11,12]. Since the shape of the absorption spectrum was not influenced by any of pH and concentrations of Fe(III) and H_2bbpen , it was found that single species is concerned in the coloration.

The metal:ligand ratio of the Fe(III)- H_2bbpen complex was determined as 1:1 by applying Job's continuous variation method. Furthermore, this colored complex was extracted perfectly into chloroform with perchlorate as counter anion, while not extracted with nitrate or chloride. Namely, this colored complex can be regarded as $\text{Fe}(\text{bbpen})^+$ and its molar decadic absorption coefficient (ϵ) was calculated as 4.3×10^3 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ($\lambda_{\text{max}} = 560$ nm).

On $\text{pH} < 2$, the hydrolysis of Fe^{3+} is negligible [11,12] and H_2bbpen is converted to $\text{H}_4\text{bbpen}^{2+}$ [9,10]. Therefore, the complexation equilibrium and its equilibrium constant (K) in this condition can be expressed as follows:



$$K = \frac{[\text{Fe}(\text{bbpen})^+][\text{H}^+]^4}{[\text{Fe}^{3+}][\text{H}_4\text{bbpen}^{2+}]} \quad (2)$$

Figure 2 shows the plot of $\log \{[\text{Fe}(\text{bbpen})^+]/[\text{Fe}^{3+}][\text{H}_4\text{bbpen}^{2+}]\}$ versus pH, which gave a straight line with a slope very close to 4. From the result, the colored species was clarified as $\text{Fe}(\text{bbpen})^+$ and the value of $\log K$ was determined as -1.2 ± 0.1 . With using the obtained constant and pK_a values of H_2bbpen [9], the logarithmic stability constant of $\text{Fe}(\text{bbpen})^+$ ($\log \beta_1$, $\beta_1 = [\text{Fe}(\text{bbpen})^+]/[\text{Fe}^{3+}][\text{bbpen}^{2-}]$) was calculated as 32.6 ± 0.1 .

The absorbance reached maximum value within 100 min at 20 °C, which was shortened to 5 min by warming the solution using a water bath at 50 °C. To the contrary, the maximized absorption continued for more than a year. This surprisingly high stability seems to be originated from the enhancement of ligand-to-metal charge transfer (LMCT) from phenolate- O^- to Fe^{3+} by additional coordination of pyridine-N. In actual, the use of N,N' -bis(2-hydroxyphenylmethyl)-1,2-ethanediamine (H_2bbsen) instead of H_2bbpen showed rapid fading of purple coloration by complexation within 1 min.

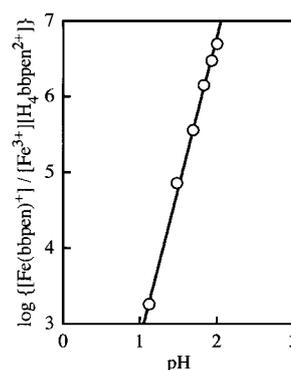


Fig. 2. Relationship between $\log \{[\text{Fe}(\text{bbpen})^+]/[\text{Fe}^{3+}][\text{H}_4\text{bbpen}^{2+}]\}$ and pH. Initial concentrations of Fe(III) and H_2bbpen were 1.67×10^{-4} mol dm^{-3} . Measured wavelength was 560 nm. Solid line, of which the slope is 4, was obtained by the least square fit.

Potential use of H_2bbpen for the determination of iron(III)

On the optimized condition, the calibration graph was linear in the range of 5×10^{-6} – 2×10^{-4} mol dm^{-3} (0.3 – 12 $\mu\text{g cm}^{-3}$) of Fe(III). The detection limit calculated by using the 3σ criterion was 3×10^{-6} mol dm^{-3} (0.2 $\mu\text{g cm}^{-3}$).

The effect of diverse foreign metal cations on the determination of Fe(III) was examined. The tolerance limit, which was defined as the amount causing an error $\pm 3\%$ in the absorbance, was more than 100-fold amount of Fe(III) for most of cations such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mn^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Al^{3+} , Ga^{3+} and Y^{3+} . Positive interference of Ni^{2+} (tolerance limit = 20-fold), Cr^{3+} (5-fold) and Cu^{2+} (0.75-fold) is originated from the absorption of their hydrated ions themselves and it is convinced that the interference can be minimized by using sample solution itself as blank instead of pure water. In addition, Co^{2+} (tolerance limit = 2.5-fold) seemed to be oxidized partly to Co^{3+} forming colored complex $\text{Co}(\text{bbpen})^+$ in this system [7]. Furthermore, c.a. 20% of Fe^{2+} was oxidized and formed unexpected $\text{Fe}(\text{bbpen})^+$ complex and the tendency was enhanced on $\text{pH} > 2.5$.

This method was applied to the determination of Fe(III) in tap water. Although its Fe(III) content was lower than 0.3 $\mu\text{g cm}^{-3}$ (determined as 0.22 $\mu\text{g cm}^{-3}$ by ICP-AES), that of the sample adding 1.50 $\mu\text{g cm}^{-3}$ of Fe(III) was measured as 1.77 ± 0.01 $\mu\text{g cm}^{-3}$ ($n = 8$), agreed with that by ICP-AES (1.78 $\mu\text{g cm}^{-3}$).

This system has some room for improvement. Particularly, further derivatization of the ligand is very important to enhance the absorption of its Fe(III)-complex and to accelerate the complexation reaction, which are necessary for the combination of this system with high-performance automated analysis such as flow-injection analysis.

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