Spectrophotometric Determination of Hydrogen Molecule by Redox Reaction of Ferric and Cupric Using Platinum Catalyzer

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Abstract: Simple methods for the determination of hydrogen molecule in water are developed. These methods are based on the redox reactions between metal ions such as ferric ion and cupric ion with hydrogen molecule in the presence of colloidal platinum. The released ferrous ion was developed with *o*-phenanthroline, bathophenanthrolinedisulfonate and Ferrozine, on the other hand cuprous ion was developed with bathocuproinedisulfonate. In these methods, ferric ion is superior than cupric ion because of its sensitivity and stoichiometric reaction with hydrogen molecule. The hydrogen molecule proved to decompose hydroxy radical released from Fenton reaction by spectrofluorometry.

Key words: Molecular hydrogen, colloidal platinum, *o*-phenanthroline, Ferrozine, bathocuproinedisulfonate spectrophotometry.

1. Introduction

Hydrogen water was known to be most effective wet cleaning of silicone surfaces [1] and used for nutrient solution of Komatsuna plants [2]. On the other hand, many studies have been made for influence of health. Ohsawa, et al. [3] reported that hydrogen water can efficiently remove active oxygen, therefore, hydrogen water can be expected for treatment of cerebral infarction. Shimouchi, et al. [4, 5] reported when 7 adults took hydrogen water, 40% hydrogen has been consumed by acting with hydroxyl radicals. Although hydrogen water has attracted attention in these ways, there are surprisingly few methods for easily measuring the hydrogen molecule concentration.

There are some methods for determination of hydrogen molecule concentration by gas chromatography [6], conducting electrolyte [7], voltammetric [8], amperometric [9]. However, no study has been made concerning spectrophotometric determination of hydrogen molecule in water. So, author proposed the

new spectrophotometric method using colloidal platinum as oxidative catalyzer of hydrogen molecule for reduction of ferric ion. The produced ferrous ion was developed with *o*-phenanthroline and the complex (ferroin) formed was determined spectrophotometrically [10]. In this paper, authors try to use another developing reagent for ferrous ion, and so on try cupric ion for oxidative ion. The cupric ion reduced to cuprous ion and developed with bathocuproinedisulfonate. Reaction of hydrogen molecule between hydroxy radical released from Fenton reaction was also performed.

2. Experimental

2.1 Materials and Reagents

Spectrophotometer measurements were made with a Shimadzu UV-1800 spectrophotometer using 1 cm glass cells. Spectrofluometric measurements were made with a Shimadzu RF-5300pc spectrofluorophotometer using 1 cm 4-sided transparent quartz cell. A TOA HM-30V was used for pH measurement. MAGICPOT hydrogen generator

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CCMP was used for preparation of hydrogen water using drinking water (total hardness 50 mg/L). The average of concentration of hydrogen molecule in this water is near 0.5 mg/L. And the concentration was measured using dissolved hydrogen meter KM2100DH.

All reagents were of analytical grade and the solutions were prepared with deionized water from an ELGA PURELABOTION-S type.

Ferric solution: Weigh 0.362 g of ferric nitrate enneahydrate and add 2.5 mL of 1 mol/L hydrochloric acid and dilute with water to 250 mL.

Cupric solution: 0.499 g of cupric sulfate pentahydrate was dissolved in 100 mL of water, and the solution was diluted tenth fold with water.

Also 1×10^{-3} mol/L of platinum nanoparticle dispersion solution was prepared with diluting with water using 10 mM of platinum nanoparticle dispersion from Renaissance Energy Research Ltd.

Developing reagent for ferrous ion: 2 g of *o*-phenanthroline dichloride monohydrate, bathophenanthrolinedisulfonic acid disodium salt, and 3-(2-pyridyl)-5,6-bis(4-sulfophenyl)-1,2,4-triazine disodium salt hydrate (Ferrozine) were dissolved in 100 mL of water.

Developing reagent for cuprous ion: 0.2 g of bathocuproinedisulfonic acid, disodium salt was dissolved in 250 mL of water.

pH 6.15 buffer solution: 10.2 g of MES (2-Morpholinoethanesulfonic) acid monohydrate was dissolved in water and the pH was adjusted with sodium hydroxide solution and made up 250 mL with water.

pH 5.8 buffer solution: 2.13 g of MES acid, monohydrate was dissolved in water and the pH was adjusted with sodium hydroxide solution and made up 250 mL with water.

Fenton reaction: The reaction was carried out using 100 μ M ferric ion, 10 μ M HPF (Hydroxyphenyl Fluorescein) solution diluted with 0.1 M phosphate buffer solution (pH 7.4), and 1 mM hydrogen peroxide solution.

2.2 Standard Procedure by Ferric Reduction

Transfer 5 mL sample solution into volumetric flask. Add 0.5 mL of ferric solution, 0.15 mL of platinum nanoparticle dispersion solution, 2 mL of developing reagent solution, 0.5 mL of pH 6.15 buffer solution and dilute with water to 10 mL. The absorbance was measured with 1 cm cell at 510 nm (*o*-phenanthroline), 533 nm (bathophenanthrolinedisulfonate) and 562 nm (Ferrozine).

2.3 Standard Procedure by Cupric Reduction

Transfer 5 mL sample solution into volumetric flask. Add 0.5 mL of cupric solution, 1 mL of platinum nanoparticle dispersion solution, 0.5 mL of developing reagent solution, 2 mL of pH 5.8 buffer solution and dilute with water to 10 mL. The resultant solution was measured with 1 cm glass cell at 485 nm.

2.4 Reaction of Hydroxyl Radical and Hydrogen Molecule

Preparation of hydroxyl radical was followed. Add 1.0 mL ferric ion, 1.0 mL HPE solution, 1.0 mL hydrogen peroxide, and dilute with water to 10 mL. The resultant solution was measured using 1 cm 4-sided transparent quartz cell with spectrofluorophotometer at $\text{Ex} = 490$ nm and $\text{Em} = 490$ nm. The reaction of hydroxyl radical and hydrogen molecule was carried out after addition of 1 mL 0.5 ppm hydrogen molecule. The fluorescence intensity of solution is also measured.

3. Results and Discussion

3.1 Determination Hydrogen Using Ferric ion

Ferrous ions are determined spectrophotometrically with *o*-phenanthroline, bathophenanthrolinedisulfonate and Ferrozine. The data of the coefficient of molar absorptivities (ϵ) using these reagents are 1.1×10^4 [11], 2.24×10^4 [12] and 2.79×10^4 [13]. If the redox reaction with ferric ion and hydrogen molecule is follows,

The molar absorptivities for hydrogen molecule are exposed to two-fold against these values, however, in the case of bathophenanthrolinedisulfonate, the value was smaller than expected value. From these results, Ferrozine was most sensitive reagent (Table 1).

3.2 Determination of Hydrogen Using Cupric Ion

3.2.1 Influence of Colloidal Platinum

The surface of colloidal platinum provides reaction field, and it suggests that it promotes redox reaction of cupric ion and hydrogen molecule. Fig. 1 indicates the influence of colloidal platinum solution on reduction of cupric ion. If the colloidal platinum is not present, the absorbance of the solution is same of blank solution. Increment of colloidal platinum introduced increasing of absorbance and more than 1.0×10^{-4} mol/L of colloidal platinum concentration in the final solution indicates constant absorbance.

3.2.2 Effect of pH

The optimum pH condition of redox reaction of hydrogen molecule and cupric ion was investigated. The result is shown in Fig. 2. From this result, it was shown the maximum pH was pH 5.5. At higher pH more than pH 6, the absorbance was drastically decreased. The pH 5.5 is optimum condition of redox reaction of hydrogen and cupric ion.

3.2.3 Calibration Curve for Hydrogen Molecule in Water

Linear calibration curve was obtained using a standard procedure (Fig. 3). Beer's law is obeyed in the range of 0 to 6.5×10^{-6} mol/L. The molar coefficient for hydrogen molecule in water is 1.44×10^4 L·mol⁻¹·cm⁻¹ and exhibits an excellent linear correlation coefficient (0.993). It did not mean that 1 mol of hydrogen molecule reduced 1.14 mol of cupric ion because cuprous molar absorptivity using this reagent is 1.26×10^4 L·mol⁻¹·cm⁻¹ [14] and the blank value was 0.0748.

Table 1 Comparative study for measurement of hydrogen molecule by spectrophotometric method.

Reagents	Wavelength (nm)	Blank value	Molar absorption coefficient (ϵ) ($\times 10^4$)	
			Proposed method	Iron (II)
<i>o</i> -Phenanthroline	510	0.091	2.26	1.11 [11]
Bathophenanthrolinedisulfonate	535	0.110	4.25	2.24 [12]
Ferrozine	562	0.240	5.59	2.79 [13]

Fig. 1 The influence of concentration of colloidal platinum on reduction of cupric ion.

Fig. 2 The influence of pH condition of redox reaction of hydrogen molecule and cupric ion.

Fig. 3 Calibration curve for hydrogen molecule in water.

3.3 Reaction of Hydrogen and Hydroxy Radical

Decomposition reaction of hydroxy radical with hydrogen molecule was performed. The formation reaction of hydroxy radical was carried out by Fenton reaction. The resulted hydroxy radical was identified with HPF by spectrofluorometry. HPF was oxidized with hydroxy radical and formed fluorescent compound. Its fluorescence was measured as follows

[15]. Fig. 4 shows fluorescence wavelength and its intensity in the presence or absence of H₂O₂. From this result, hydroxy radical formation with H₂O₂ indicated formation of fluorescence compound. However, with addition of hydrogen molecule solution to hydroxy radical contained solution, the fluorescence disappeared, shown in Fig. 4.

Fenton reaction

Fig. 4 Reaction of hydrogen and hydroxy radical.

4. Conclusion

The other reagents without *o*-phenanthroline were performed in the case of ferric ion as oxidant, in these reagents Ferrozine was most sensitive for hydrogen molecule, its molar coefficient was $5.59 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. Another metal ion using cupric ion as oxidative ion for determination of hydrogen molecule was also experienced. The reagent employed was bathocuproindisulfonic acid, its molar coefficient for hydrogen molecule was $1.44 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. The method using cupric ion as oxidative ion was not so

sensitive compared to ferric ion, and stoichiometry reaction of hydrogen molecule and cupric ion was not performed. Finally, reaction of hydrogen molecule with hydroxy radical was also verified. The depression of hydroxy radical concentration was confirmed by decreasing fluorescence intensity using HPF as fluorescence reagent.

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