Interaction between silver ions and histidine*★

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Abstract

BACKGROUND: Traditionally, UV/visible spectra, conductivity, electrophoresis and other methods are commonly applied for studying the interaction of metal ions and amino acids, but UV-Vis spectroscopy and fluorescence spectroscopy for L-histidine reacted with silver ion in aqueous solution is rarely reported.

OBJECTIVE: To investigate the interaction between silver ion and histidine using UV/VIS and fluorescence spectra.

METHODS: The influence of pH, multicomponent concentration such as histidine, silver ion, formaldehyde, sodium dodecyl sulfate and trihydroxymethyl aminomethane, as well as illumination strength and time, on the interaction between silver ion and histidine were investigated, and the mechanism of reaction was also explored.

RESULTS AND CONCLUSION: Applied pH potentiometer titration method, the dissociation constants of histidine was defined 9.21. The stepwise stability constants of histidine-silver was $\log K_1$=5.56 and $\log K_2$=4.05, respectively by using half n̄ method. At 20 ℃, the electric potential of histidine-silver system was 2.10×10^{-4} V. According to pH potentiometer titration and Iob method, the compound was consisted of histidine: Ag = 2:1. Compared with histidine, histidine-silver systems reached a shoulder peak at 295.3 nm, which was assigned to conjugate double bond of imidazole ring that easily generated π-π* transition. And an absorption peak close to 242 nm can be assigned to n-π* transition of the C=O group of the histidine-silver. The fluorescence emission spectra of histidine-silver systems belonged to $^5D_0\rightarrow{}^7F_2$ electric dipole transition. Compared with reference solutions under the same conditions, it not only emitted wavelengths blue shift, but also induced fluorescence quenching. Results showed that, imidazole ring was involved in the bonding action with silver ion. The reaction process is to firstly generate six-coordination complex, secondly reduce the silver ion into ultrafine silver particles which are bound by histidine.

INTRODUCTION

L-histidine is an essential amino acid for protein synthesis and various other functions in cells and tissues, such as a precursor for histamine. The histidase gene is isolated from a human genomic library using the human histidase cDNA as a probe [1]. The interaction of metal ions to amino acids, peptides and proteins plays a very important role in biology. Metal ions with bimolecular in solution may cause a series of chemical processes such as catalysis, electron transfer, O_2 transport and stabilization, *etc* [2]. Furthermore, metal ions play a very crucial role in the organism with three-dimensional biological structures [3]. The bio-inorganic chemistry of the silver (I) ion is rich and fascinating. The silver (I) ion has long been used as a bactericide in the form of eye drops for newborns [4-5]. Some of its complexes display remarkable antimicrobial activities [6-7]. The metallothioneins, a class of small proteins believed to be responsible for heavy-metal detoxification in mammals, exhibit very high affinity for silver (I) [8-10]. Simple and complex 2-alkylhistamines have been of interest for more than thirty years as potential histamine agonists and/or antagonists [11-12]. The involvement of histamine in the allergic response has stimulated interest in the synthesis of numerous antihistamines as well as the synthesis of different histamine derivatives designed to study various histamine receptors. Recently, several of these alkylbioimidazoles have been explored as antitubercular agents [13]. Data on the influence the solution's ionic composition and amino acids (histidine, methionine) have on the anodic dissolution of silver are presented [14]. For amino acids that contain nitrogen-bearing side-chains, *i.e.* histidine, tryptophan, their relative silver (I) ion binding energies are larger than their corresponding copper (I) ion binding energies. This effect is likely due to more favorable binding because of Ag (I) ion larger size [15-18] and softer properties relative to Cu (I). The vibrational study of amino acids adsorbed on metal surface is quite complex, given that the species giving rise to the SERS records may be the anion, the cation, or even the zwitterions. Moreover, the interaction with the metal ion may take place through only one or both functional groups or even through an additional functional group present in the side chain. On the other hand, immobilization of silver ion for metal affinity chromatography [19], as well as interaction between the surface of the silver nanoparticles prepared by γ-irradiation and organic molecules containing thiol group [20], have been studied. But the photochemistry for interaction silver with histidine is rarely studied. Our group have previously recorded and analyzed the interactions of silver (I) with BSA, Hb, and γ-Gb, Trp, *etc* [21-24], as well as the photochemistry properties on reactions of amino acids with silver [25]. The present work is aimed at the investigating the interaction, photochemistry properties, and mechanism of the silver with histidine at the molecular level using spectroscopic techniques, as well as the dissociation constants of histidine, stability constants of histidine-silver coordination compound, electrokinetic's potential of histidine-silver system were estimated by pH potentiometer titration, electrophoresis methods respectively.

MATERIALS AND METHODS

Instrumentation

The fluorescence spectra were recorded with RF-540 spectrophotometer fitted with a 150W Xenon lamp. A slot width of excitation or emission was 10 nm, scan

velocity was fast, and the sensitivity was low. The UV/VIS spectra were recorded with UV-265 and Agilent 8453 ultraviolet-visible spectrophotometer. The illumination was measured with a digitally illuminometer (TES-1330A, Taiwan), and the light was focused on the cassette by a jaws, which in control. An 818 model acidometer (Orion CO., USA) has been check up pH of medium. The electrokinetic's potential was performed with electrophoresis apparatus (DYY-III-A, Beijing).

Chemicals

The silver nitrate ($AgNO_3$, 99.9%) was purchased from Shanghai Chemicals Co.Ltd. (China), it is 0.03 mol/L of Ag $(NH_3)_2NO_3$ solution beforehand prepared. The histidine was obtained from Sigma-Aldrich Co. The sodium dodecyl sulfate (SDS) was obtained from Inorganic Chemical Co. Ltd. (Chong-Qing, China); trihydroxymethyl aminomethane (Tris) as a buffer was purchased from Chemical Co.Ltd. (Beijing, China). Used chemicals were of analytical-reagent grade. All chemical were used without further purification.

Procedures

The aqueous histidine-silver has been prepared by successively added 3.6 mL of 0.02 mol/L histidine solution, 0.8 mL of 0.03 mol/L $Ag(NH_3)_2NO_3$, 1.2 mL of 1%(*w*/*v*) Tris buffer solution, 0.4 mL of 4%(*w*/*v*) SDS, and 1.0 mL of 0.1%(*v*/*v*) HCHO in 10 mL of centrifugal tube be provided with scale, then adjusted to pH values with HNO_3 or NaOH, and reacted for 90 minutes after the vibration has been fairly well-distributed, finally added 1.5 mL of 12%(*v*/*v*) HAC to stop reaction and made the final volume up to 10 mL. The sample was characterized by means of UV/VIS and fluorescence spectra.

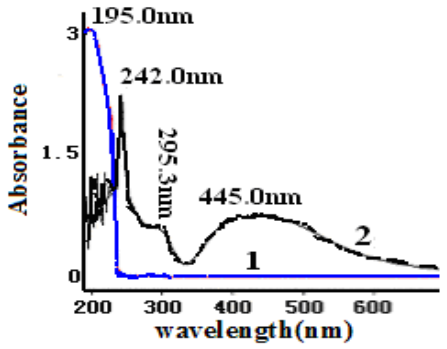
RESULTS AND DISCUSSION

The UV/VIS spectra of histidine-silver

Figure 1 shows the UV/VIS spectra of blank histidine and histidine-silver. The histidine solution was observed with noticeable absorbance at 195 nm, which was assigned to the conformation of histidine and n-δ* transition of lone-pair electron of amino-group due to imidazole ring has tautomerism [26]. Compared with histidine, histidine-silver system was observed a shoulder peak at 295.3 nm, which was assigned to conjugate double bond of imidazole ring that easily generated π-π* transition. And an absorption peak could be assigned to n-π* transition of the C=O group of the histidine-silver close to 242 nm. Results of the UV/VIS spectra demonstrated that, the new species are generated and the colors of solution are changed from colorless, orange-red to brown-red. The reaction process was that silver (I) with histidine first come into being complex, then Ag^+ reduced to Ag^0 by HCHO which acted as a reducing agent, thus it was bound by histidine, and consequently appeared broad and smooth band in the range from 400 nm to 500 nm.

Fluorescence emission spectra of histidine-silver

Table 1 has listed the excitation and emission wavelengths of histidine-silver systems as well as its relative fluorescence intensities. It had been found that emission wavelengths of histidine reference and histidine-silver were longer than histidine solution. Also we noticed that the relative fluorescence intensities of complexes were lower than reference solution; this phenomenon belonged to static fluorescence quenching. As is known to all, protein consists of twenty amino acids, in which only Trp, Try and Phe have internal fluorescence and the ratio of its relative intensities is 100: 9: 0.5, respectively [27].



(1) Histidine solution (reference: H_2O); (2) Histidine-silver (reference: histidine, Tris, SDS, HCHO, and HAC)

Figure 1 The UV/VIS spectra of histidine-silver

Table 1 Fluorescence emission spectra of histidine-silver system

Histidine	Excitation wavelength (nm)	Emission wavelength (nm)	Fluorescence intensity
Solution	279.2	313.1	5.3
Reference	282.3	340.7	39.7
His-Ag	280.8	336.9	16.1

Reference includes histidine, Tris, SDS, HCHO, and HAC

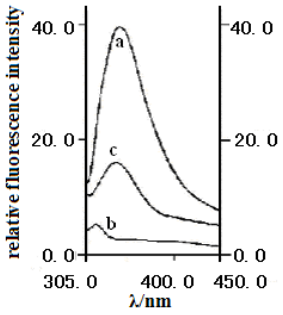
Although histidine has no fluorescence characteristic, its reference solution has fluorescence due to Tris, SDS, HCHO and HAC are added, the cause as follows: ① System is changed. The repulsive interaction of $-NH_2-NH_2-$ and of intra-intermolecular hydrogen bond all increase by adding SDS and HCHO, then form random coil structure, thus π-π* transition energy decrease and generate fluorescence. ②The ligand for amino acid absorb light energy, then the energy is transferred to central silver (I) ion through exchangeable role of resonance that results in silver (I) generate fluorescence. The fluorescence emission spectra of histidine-silver systems belong to $^5D_0 \rightarrow {}^7F_2$ electric dipole transition. With generation of new complexes, not only the emission wavelengths show blue shift as compared with reference solutions, but also fluorescence quenching occurs (Figure 2). It is likely that n-π* and π-π* transitions need more energies after histidine reaction with silver (I).

Effect of pH

The change o f the Soret bands in UV/VIS spectra for histidine-silver system with pH

Figure 3 provides the changes of the Soret bands in UV/VIS spectra for histidine-silver with pH. The maximal absorbance at Soret band increased with increasing pH from 3.08 to 6.05, but it generally decreased with pH was more than about 6.05. This interpretation is that the coordination seems to be saturated at

pH 6.05. Generally, the coordination of the amino acid to silver (I) ion seems to occur through the amino-group or carboxy group, forming two or four coordinate complexes. But histidine contains imidazole group that three-stage nitrogen atom has an unshared-pair electron, therefore, it easily reacts with metal ion and forms coordination bond [28-29]. Based on the results, it is deduced that histidine-silver is six coordinate complexes (Figure 4).



(a) Reference solution (include: histidine, Tris, SDS, HCHO, and HAC); (b) Histidine solution; (c) Histidine-silver system

Figure 2 The fluorescence emission spectra of histidine-silver system

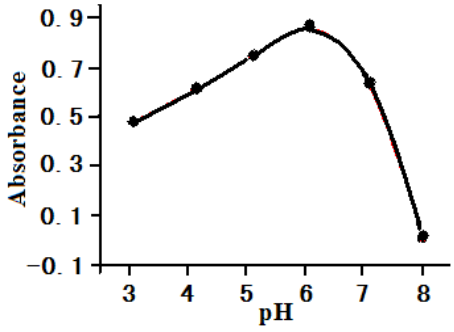


Figure 3 The change of the Soret bands in UV/VIS spectra for histidine-silver system with pH

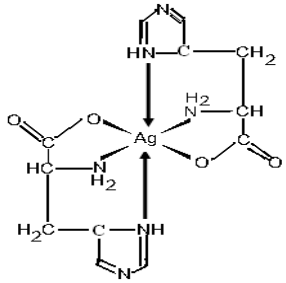


Figure 4 Proposed structure of the histidine-silver complex

Potentiometer titrations

The pH dependence of the complex formations was determined by the potentiometric titrations. The 10 mL 0.01 mol/L HNO_3, 100 mL 0.2 mol/L KNO_3 (for kept ionic strength) and 4× 10^{-3} mol/L $AgNO_3$ were placed in a flask. The mixture was titrated potentiometrically with 0.04 mol/L Na-His solution. In each addition (0.2 mL), the pH electrode of the pH meter (Orion 818, USA) was dipped into the aqueous phase and pH values were measured soon after each addition of the titer. Variation of the pH, as a function of ml of the Na-His solution added, was pictured. Same procedure was applied to 0.04 mol/L histidine described as follows.

Determination of stability constants of the complexes

Simple interactions between metal (Ag^+) and ligand (L-histidine) and then equilibrium expressions were formulated as follows:

$$Ag^+ + L^- \rightarrow AgL, \quad k_1 = [AgL] / [Ag^+][L^-] \qquad (1)$$

$$AgL + L^- \rightarrow Ag(L)_2^-, \quad k_2 = [Ag(L)_2^-]/[AgL][L^-] \qquad (2)$$

The k_1 and k_2 are formation constants of the corresponding complexes. Formation function of complexes was obtained as follows:

$$\bar{n} = \frac{[AgL]+2[AgL_2]}{[Ag]+[AgL]+[AgL_2]} = \frac{k_1[L]+2k_1k_2[L]^2}{1+k_1[L]+k_1k_2[L]^2} \qquad (3)$$

Or

$$\bar{n} = \frac{C_L - \{(C_H - [H^+] + Kw[H^+]^{-1})/\bar{n}_H\}}{C_M} \qquad (4)$$

$$\frac{\bar{n}}{(1-\bar{n})[L]} = \frac{(2-\bar{n})[L]}{(1-\bar{n})} k_1k_2 + k_1 \qquad (5)$$

Where L^- represents the His; C_L and C_H are the total concentration of ligand (His) and acid, respectively, and K_w is the ion product of water. The stability constants of the complexes were calculated using half $\bar{n}$ from data of series [$\bar{n}$] and [L^-].

The protonation equilibrium of histidine (L) expressions were formulated as follows:

$$H + L = HL, \quad \beta^H_1 = [HL]/[H][L] = k^H_1 \qquad (6)$$

$$H + HL = H_2L, \quad \beta^H_2 = [H_2L]/[H]^2[L] = k^H_1 k^H_2 \qquad (7)$$

The formation function of H_2L is

$$\bar{n}_H = \frac{\sum_{j=0}^{2} j\beta^H_j [H+]^j}{\sum_{j=0}^{2} \beta^H_j [H+]^j} \qquad (8)$$

Here into

$$\beta^H_0 = 1 \qquad (9)$$

After recomposition:

$$\frac{\bar{n}_H}{(1-\bar{n}_H)[H^+]} = \frac{(2-\bar{n}_H)[H^+]}{(1-\bar{n}_H)}\beta_2^H + \beta_1^H \quad (10)$$

Where:

$$\bar{n} = \frac{C_H - [H^+] + Kw[H^+]^{-1}}{C_L} \quad (11)$$

Where C_L, C_H are total concentration of ligand (His) and acid, respectively. And K_w is ion product of water. Same, the protonation constants (*i.e.* reciprocal of dissociation constants) of the histidine (L) were calculated using half $\bar{n}$ from data of series [$\bar{n}$] and [L] (Figure 5).

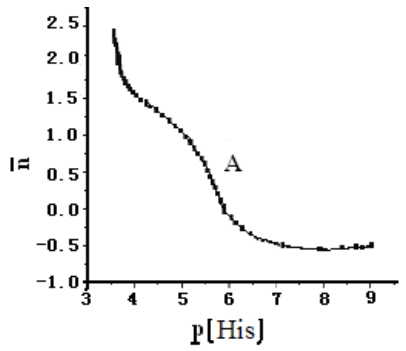


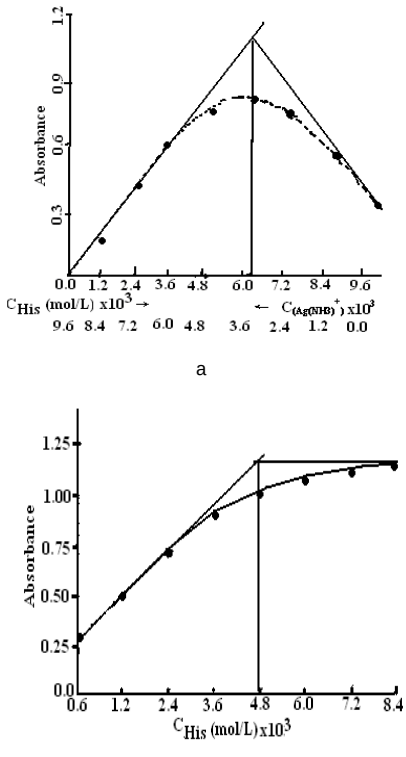
Figure 5 Plots of $\bar{n}$ *vs* p[His](-lg[His])

Applied pH potentiometer titration [30], we obtained that the dissociation constants of histidine was 9.21, which was adjacent that with research of Jia *et al*[31] and the stepwise stability constants as follows: ^{log} K_1 and ^{log} K_2 of histidine-silver were 5.56 and 4.05, respectively.

Determination of stoichiometries of the complexes

Stoichiometries of the complexes were determined using Job method (Continuous variation and mole ratio method). Two series of solutions were prepared. In the first series, the ligand (histidine) and $Ag(NH_3)_2^+$ concentration both was kept equality (0.0×10^{-3} mol/L to 9.6×10^{-3} mol/L), but was changed additive volume; In second series, the $Ag(NH_3)_2^+$ concentration was kept constant and very large (2.4×10^{-3} mol/L) while the ligand concentration was increased in a regular (1.2, 2.4, 3.6, 4.8 …$\times10^{-3}$ mol/L).

The absorbance of the solutions in each series was plotted against the concentration of the variable component (Figure 6 a, b). Two lines were obtained with different slope values. The ratio of the Ag $(NH_3)_2^+$ to ligand (mol/L) was calculated from the ratio of the slopes of the lines. In Figure 6a, the maximum at a C_{His}/C_{Ag} of equal to 0.64/0.33=2:1 was obtained, and in Figure 6b a junction of two lines was at a C_{His}/C_{Ag} of equal to 4.7×10^{-3} mol/L/2.4×10^{-3} mol/L=2:1, *i.e.* n_{Ag}/n_{His}=1:2 was obtained, both were indicated a 2:1 complex.

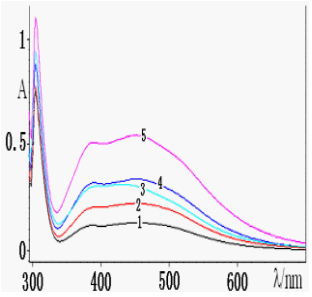


λ=445.0 nm; pH=7.05; $C(Ag(NH_3)_2^+)=2.4\times10^{-3}$ (mol/L)

Figure 6 Continuous variation (a) and moleratio (b) plots of the absorbance of histidine-silver complexes

Effect of other species ($Ag(NH_3)_2^+$, Tris, SDS, HCHO) concentrations

The maximum absorption peak of fluorescence spectra for histidine-silver was increased when [$Ag(NH_3)_2^+$] was higher than 2.4 mmol/L. The explanation was that increased concentration of [$Ag(NH_3)_2^+$] is benefit to reaction process. The effects of concentration of [Tris] and [HCHO] were little to reaction. SDS not only was surfactant but also reduced the sedimentation of silver gel when histidine reacted with silver (I), and it is benefit to the formation of complex as increased concentration of [SDS] (Figure 7).



1: 0.5%; 2: 1.0%; 3: 2.0%; 4: 3.0%; 5: 4.0%
$C_{His}=7.2\times10^{-3}$ mol/L, $C_{Ag+}=2.4\times10^{-3}$ mol/L

Figure 7 The UV/VIS absorbencies of histidine-silver in different concentrations of sodium dodecyl sulfate

Electrokinetic potential of histidine-silver system

We found that histidine-silver systems were carried on negative charges and moved to positive polar with electrophoresis method [32]. The electrokinetic's potential is expressed as:

$$\xi=4\pi\eta/D\cdot uL/E\cdot 9\times10^4 \text{ V} \quad (12)$$

Where ξ is electrokinetic's potential, and D and η are the dielectric constant (81) and viscosity (η_{20}=0.010 poise) of aqueous disperse medium respectively. E is the voltage of the two electrodes of infliction on electrophoresis tube. U is a proportion of the moving distance (cm) of solution boundary by electric field force in time *t* (sec). L is the distance (m) of two electrodes. The values of electrokinetic's potential of histidine-silver systems are summarize in Table 2. The results showed that have formed electric double layer between the silver and amino acids.

Table 2 The electrokinetic potential of histidine-silver system (20 ℃)

Aminoacid	Electrophoresis time (s)	E/v	L/m
Histidine	150	117	5.3×10^{-2}

Aminoacid	Moving distance of boundary/m	u cm/sec	ζ/V
Histidine	5.0×10^{-3}	3.33×10^{-3}	2.10×10^{-4}

Effect of illumination strength and time

The data of fluorescent spectra for histidine-silver in different illuminations is presented in Table 3. As compare with reference solution, the fluorescence intensity was minished with increasing illumination, namely fluorescence quenched. Moreover, the bigger illumination was urged to the more evidently the fluorescence quenched.

Table 3 The fluorescence emission spectra of histidine-silver system in different illumination intensities

Illumination (Lux)	Histidine-Ag		
	Excitation wave-length (nm)	Emission wave-length (nm)	Fluorescence intensity
Reference solution	281.8	340.0	33.0
0	278.9	340.3	24.9
30	278.7	340.3	23.8
300	278.6	337.9	21.4
700	279.0	339.3	18.0
1 200	279.3	338.2	13.3
3 300	269.3	346.1	10.0

$C_{His}=7.2\times10^{-3}$ mol/L, $C_{Ag+}=2.4\times10^{-3}$ mol/L

It was found that the variable tendency of UV/VIS and fluorescent spectra changes for histidine-silver in different illumination time was resemble (Figure 8 and Table 4). The maximum absorbance at Soret band increased significantly with increasing illumination time from 30 minutes to 120 minutes, but the relative fluorescence intensity decreased (Table 6). It showed that the coordination was complete and the complex was stable as illumination time increased. The difference was that the effect of ultraviolet light was greater than visible light, the cause of it was ultraviolet light can provide with more energies which was benefit to reaction in the same illumination.

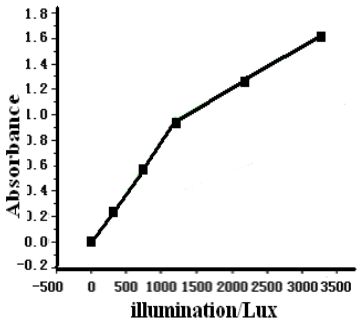


Figure 8 The UV/VIS spectra of histidine-silver systems in different illuminations

Table 4 The UV/VIS spectra of histidine-silver system in different illumination time (600±20 Lux, $C_{His}=7.2\times10^{-3}$ mol/L, $C_{Ag+}=2.4\times10^{-3}$ mol/L)

Light	Time	30 min	45 min	60 min	75 min
Visible	λ_{max}/nm	443.4	447.0	447.4	445.4
	A_{max}	0.085	0.276	0.385	0.385
Ultraviolet	λ_{max}/nm	459.8	446.6	449.6	458.8
	A_{max}	0.111	0.316	0.328	0.596

Light	Time	90 min	105 min	120 min
Visible	λ_{max}/nm	455.6	456.2	460.8
	A_{max}	0.571	0.698	0.915
Ultraviolet	λ_{max}/nm	452.2	455.0	459.4
	A_{max}	0.607	0.906	1.135

The present study showed that the reaction belonged to light-assistance chemical reaction. It had been pointed out halogenation's silver or silver compound must absorb photo energy if it was photosensitized. According to photochemistry principle, halogenation's silver absorb a photo, and then generate an electron-hole pair, thus carboxy group is capture agent of hole [33-34].

The fluorescence quenching curve and quenching constant of histidine-silver

The fluorescence quenching process is divided dynamic and static quenching. The interaction between quencher with excited state molecule of fluorescence substance lead to dynamic quenching, and the process adhere to Stern-Volmer equation [35]:

$$F_0/F=1+K_q\tau_0C_Q=1+K_{sv}C_Q \quad (13)$$

Where F_0, F are respectively fluorescence intensities when quencher is not added it and added it, K_q is bimolecular quenching rate constant, τ_0 is mean life of fluorescence molecule with no quencher (the τ_0 of the macromolecule is about is 10^{-8} s) [36]. $K_{sv}=K_q\tau_0$, it is Stern-Volmer quenching constant, and C_Q is concentration of quencher Q.

Table 5 The fluorescence emission spectra of histidine-silver system in different illumination time

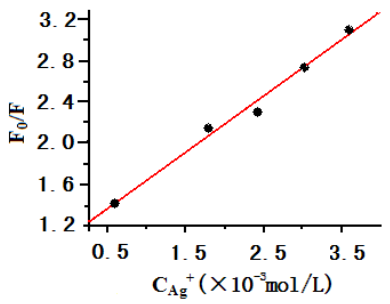
Time (min)	Ultraviolet light His		
	Excitation wavelength (nm)	Emission wavelength (nm)	Fluorescence intensity
Reference	281.6	340.5	32.8
30	278.1	338.3	25.0
45	279.5	337.1	20.6
60	278.9	337.7	20.2
75	279.7	336.5	16.1
90	279.9	336.0	16.2
105	279.7	335.4	14.0
120	279.2	336.3	11.8

Time (min)	Visible light His		
	Excitation wavelength (nm)	Emission wavelength (nm)	Fluorescence intensity
Reference	281.6	340.0	32.8
30	278.4	339.7	24.0
45	278.7	336.7	21.5
60	279.5	336.0	18.9
75	279.1	337.4	18.7
90	279.0	336.6	16.5
105	279.0	337.2	15.3
120	279.0	338.2	13.3

Table 6 Stern-Volmer quenching constant of the histidine-silver system

Linear regression equation	$F_0/F=2.102+5.427\times10^2 C_Q$
R	0.995 6
$K_{sv}(\times10^2\ L\cdot mol^{-1})$	5.427
$K_q(\times10^{10}\ L\cdot mol^{-1}\cdot S^{-1})$	5.427

We obtained that K_{sv} on the basis of the slope of quenching curve, and calculated K_q (Figure 9), the results were listed in Table 5. It is found $K_q>2.0\times10^{10}$ L•mol^{-1}•s^{-1} of the dynamic quenching rate constant that showed the collision and diffusion do not cause the fluorescence quenching function of silver (I) ion with Histidine, but the formation of histidine-silver complex results in the fluorescence quenching, this phenomenon belongs to static quenching.



λ_{ex}=281 nm; λ_{em}=337 nm; pH=6.08; $C_{(His)}=7.2\times10^{-3}$ mol/L

Figure 9 The Stern-Volmer plot for the histidine-silver

DISCUSSION

In the study, it has been found that many conditions have influence on the reaction of histidine with silver (I) ion, the influential degrees all relate to the categories and structures of amino acids, and reaction surroundings. Such as pH of medium, the concentration of Ag $(NH_3)_2^+$ and amino acid, illumination strength and time have the greatest influence on the reaction than the concentration of HCHO, SDS and Tris, *etc*. Histidine contained an imidazole ring, with silver (I) formed six coordinate complex. Previous studies rarely noticed it. The reaction process was that silver (I) with histidine firstly formed new complex, then Ag^+ was reduced to Ag^0 which was bound by histidine, thus appeared broad and smooth band from 400 nm to 500 nm in UV/Vis spectra. The results showed that the reaction of histidine with silver (I) ion was a thermodynamics spontaneous process without additional energy, but when light introduced into the system the reaction rate would be significantly changed. There processes are light-assistance chemical reactions. The studies point out the optimum condition for the interaction between histidine with silver (I) as follows: pH is about 6.05, the concentration of histidine was up to 7.2 mmol/l, $Ag(NH_3)_2^+$ up to 2.4 mmol/L, Tris up to 1.0%, SDS up to 4.0%, HCHO up to 0.08%, reaction time is 90 minutes, illumination intensity is higher than 300 Lux.

The chemical functional groups such as the carboxylate anion and the amidogen from of histidine play an important part in binding the Ag^+. The mechanism of the Ag^+ with histidine involves a redox course; the soluble Ag^+ is reduced to the elemental Ag^0 by the formaldehyde. The results of the experiment is believed that silver (I) could coordinate with oxygen atom of α -carboxy group, nitrogen atom of α-amino-group and of imidazole ring.

REFERENCES

[1] Frausto da Silva JJR, Williams RJP. The Biological Chemistry of the Elements. Oxford: Clarendon Press, 1991.
[2] Lippard SJ, Berg JM. Principles of Bioinorganic Chemistry California: Moll Valley. 1994.
[3] Petering HG. Pharmacology and toxicology of heavy metals: Silver. Pharmac. Ther Part A 1. 1976:127-130.
[4] Wigley RA, Brooks RR. In noble metals and biological systems. CRC: Boca Raton. 1992:277-297.
[5] Nomiya K, Kondoh Y, Nagano H, et al. Characterization by electrospray ionization (ESI) mass spectrometry of an oligomeric, anionic thiomalato-silver (I) complex showing biological activity. J Chem Soc Chem Commune. 1995;58:1679-1680.
[6] Nomiya K, Onoue KI, Kondoh Y. Synthesis and characterization of oligomeric, anionic thiomalato-silver(I) complexes with biological activities. Polyhedron.1995;14(10):1359-1367.
[7] Narula SS, Mehra RK, Winge DR, et al. Establishment of the metal-to-cysteine connectivities in silver substituted yeast metallothionein. J Am Chem Soc. 1991;113:9354-9358.
[8] Stillman MJ, Presta A, Gui Z, et al. Spectroscopic studies of copper, silver and gold-metallothioneins. 1994;1(5-6):375-393.
[9] Gui Z, Green AR, Kasrai M, et al. Sulfur K-Edge EXAFS Studies of Cadmium-, Zinc-, Copper-, and Silver-Rabbit Live Metallothioneins. J Inorg Chem. 1996;35(22):6520-6529.
[10] Schwartz JC, Lampart C, Rose C. Histamine formation in rat brain in vivo: Effects of histidine loads. J Neurochem. 1972;19:801-810.
[11] Zingel V, Leschke C, Schunack W. Developments in histamine H1-receptor agonists. Prog Drug Res. 1995;44:49-85.
[12] Meindl W, Friese-Kimmel A, Lachenmayr F, et al. The effect of agonists and antagonists of histamine H1- and H2-receptors on the growth of Mycobacterium tuberculosis H 37 Ra. Arch Pham. 1990;323(5):267-272.
[13] Tarasevich MR, Chernysheva LS, Bogdanovskaya VA, et al. Electrooxidation of silver in the presence of some amino acids. Russan J Electrochem. 2001;37(4):440-442.

[14] Cromer DT, Larson AC, Roof Jnr RB. The crystal structure of CuCN.NH3. Acta Crystallogr. 1965;19:192-197.
[15] Yamaguchi T, Lindqvist O. The crystal structure of diammine silver nitrate, Ag $(NH_3)_2NO_3$, at 223K. Acta Chem Scand. 1983;37(8): 685-689.
[16] Agustı´n Pe´rez-Cadenas, Rafael Lo´ pez-Garzo´ n, Luz Godino-Salido, et al. The reactivity of N-2-(4-amino-1,6-dihydro-1-methyl-5-nitroso-6-oxo-pyrimidinyl)-L-histidine towards silver(I) and zinc(II) ions. Trans Met Chem. 2002;27:184-190.
[17] Hossain Z, Huq F. Studies on the interaction between Ag and DNA. J Inorganic Biochem. 2002;91(2):398-404.
[18] Suh JS, Dilella DP, Moskovits M. Surface-enhanced raman spectroscopy of colloidal metal systems: a two-dimensional phase equilibrium in p-aminobenzoic acid adsorbed on silver. J Phys Chem. 1983;87(9):1540.
[19] Choi SH, Lee SH, Hwang YM, et al. Interaction between the surface of the silver nanoparticles prepared by γ-irradiation and organic molecules containing Thiol group. Rad Phys Chem. 2003;67:517-521.
[20] Li L, Zhang CP, Shen DJ. Preparation and characterization of polymeric ultrafine particles on Hb-SDS-Ag hydrogeles. Guang Pu Xue Yu Guang Pu Fen Xi. 2002;22(3):501-503.
[21] Zhang CP, Zhang WIR. Raman and UV/VIS spectroscopic studies on some proteins with silver (I) -copper (II) ion complexes. Huaxue Shiji. 1999;21(1):1-14.
[22] Zhang CP, Xia M. The Formation and spectra of the proteins-silver-copper complexes. Chin Spectra Spectra Anal. 1996;16(5):43-49.
[23] You YH, Zhang CP. The photochemistry properties on interaction silver with tryptophan. Spectrochim Acta A Mol Biomol Spectrosc. 2008;69(3):939-946.
[24] Xiao ZD, Zhang CP, Shen DJ. The photochemistry properties on reactions of amino acids and silver. Ganguang Kexue yu Guanghuaxue. 2005;23(3):209-217.
[25] Guo YJ. Spectrophotometric Technique and Its Applied in Biochemistry. Beijing: Academic Press. 1987:20.
[26] Tang SH, Huang JB. Study on the interaction of gelatin with transition metal ions. Huaxue Xuebao. 2001;59(8):1258-1264.
[27] Hua WT. Heterocyclic Chemistry. Beijing: Beijing University Press. 1990.
[28] Shao MZ. Bioinorganic Chemistry. Beijing Extractive Industry Press. 1988.
[29] Wang BK. Middle Inorganic Chemistry Experiment. Nanjing: Nanjing University Press. 1988:34.
[30] Lu W, Apostoll I, Qasiml MA, et al. Binding of amino acid side-chains to S1 cavities of serine proteinases. Mol Biol. 1997;266(2):441-461.
[31] Glasston S. An introduction to electrochemistry, Jia LD, Li DC, Zhang LK, et al.(Chinese translate). Beijing: Silence Press. 1959:637.
[32] Xu SL, Xu QH, Tian YC, et al. A Series of Books on Inorganic Chemistry. Beijing: Science Press.1995:556.
[33] Guo H, Xia PJ. The translation and using of the holes in the image formation of AgX microcrystals. Ganguang Kexue yu Guanghuaxue. 2003;21(5):398-398.
[34] Ma GB, Gao F, Ren BZ, et al. Study on the interaction of human serum albumin and drug molecules by the fluorescence method. Huaxue Xuebao. 1995;53:1193-1197.
[35] Banerjee D, Mandal A, Mukherjee S. Excited state complex formation between methyl glyoxal and some aromatic bio-molecules: a fluorescence quenching study. Spectrochim Acta A Mol Biomol Spectrosc. 2003;59(1):103-109.
[36] Hua JC. Microstructure Analysis of Polycrystalline X-ray Diffraction. Shanghai: Hua-Dong normal Uni Press. 1989: 155-180.

组氨酸和银离子间的相互作用*★

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摘要

背景：以往研究多采用紫外/可见光谱、电导和电泳等方法研究金属离子与氨基酸之间的作用，但以 UV-Vis 光谱、荧光光谱方法研究 L-组氨酸同银离子在水溶液中反应的机制少见报道。

目的：采用 UV-Vis 光谱、荧光光谱方法研究 L-组氨酸同银离子的作用机制。

方法：用 UV-Vis、荧光光谱法研究了组氨酸同银离子间的相互作用，考察介质的 pH、Ag^+ 离子、组氨酸、甲醛、十二烷基硫酸钠、三羟甲基氨基甲烷浓度以及光照强度和光照时间等条件对组氨酸同 Ag^+ 离子作用的影响，探究反应机制。

结果与结论：pH 电位滴定法测定 L-组氨酸离解常数为 9.21，用半 n̄ 法求得组氨酸-Ag 的逐级稳定常数为 $\log K_1$=5.56, $\log K_2$=4.05，20 ℃时组氨酸-Ag 体系的电动电位为 2.10×10^{-4} V。根据 pH 电位滴定法和 Iob 法确定该配合物的组成为组氨酸：Ag=2：1。同组氨酸相比，组氨酸-Ag 体系在 295.3 nm 有一肩峰，它对应于咪唑环产生的π -π * 跃迁。而 242.0 nm 左右出现的吸收峰属于组氨酸中 C=O 的 n-π * 跃迁。组氨酸-Ag 体系产生的荧光发射光谱归属为 $^5D_0\rightarrow{}^7F_2$ 电子偶极跃迁。同相同条件下的参比液相比，不仅发射波长蓝移，而且导致荧光猝灭。结果表明，组氨酸中的咪唑环参与了同银离子的成键作用。组氨酸同银离子发生反应后，首先生成六配位配合物，然后银离子再被甲醛还原为超细银粒而被组氨酸所包裹。

关键词：组氨酸；银；紫外-可见光谱；荧光光谱；光化学；生物材料基础实验

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