Determination of Trace Silver(I) in Basic Aqueous Solution by Electrochemiluminescence of a New Reagent 6-(2-Hydroxy-4-Diethylaminophenylazo)-2,3-Dihydro-1,4-Phthalazine-1,4-Dione

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The electrochemiluminescence (ECL) of a new reagent 6 (2 hydroxy 4 diethylaminophenylazo)-2,3-dihydro-1,4 phthalazine 1,4-dione (HDEA) in a basic aqueous solution was studied by using the apparatus designed by ourselves. Trace amounts of silver (I) shows a significant effect on the efficiency of light emission of HDEA during a positive trigonometrical wave pulse was exerted on the solution. The linear relationship between the light intensity and the concentration of silver (I) occurs in the range of 5.0×10^{8} to 3.0×10^{-6} mol/L Ag(I) in a medium of KOH-KCl-HDEA (pH = 12.8). The detection limit of the method is 2.0×10^{8} mol/L Ag(I), and the r. s. d. for 1.0×10^{-7} mol/L Ag (I) is 5%. Of 21 metal ions concerned, only nickel(II), cerium(IV) and cobalt(II) interfere the silver detection seriously; I and Br also have some interference.

Keywords Electrochemiluminescence, Reagent, Silver, 6 (2 Hydroxy 4 diethylaminophenylazo) 2,3 dihydro 1,4 phthalazine 1,4 dione

Introduction

Generally, metal ions have a catalytic action on the chemiluminescence of luminol or its derivatives in basic aqueous solutions. In the presence of excess luminol (or its derivatives) and hydrogen peroxide, the chemiluminescence intensity is proportional to the metal ion concentration, so that trace metal ions can be determined[1]. There are only a few reports on using the ECL method to determine the concentrations of metal ions[2,3], of which luminol has been used as a luminescence reagent predominately. Lin Jinming reported the investigation of electrochemiluminescence of the new reagent 6 (2 hydroxy 4 diethylaminophylazo)-2,3-dihydro 1, 4 phthalazine- 1, 4 dione (HDEA)[4], and the mechanism of the ECL of HDEA was also discussed in that paper. In the present paper,

we study the electrochemiluminescence properties of HDEA by using metal ions as the cat alyst, and describe a sensitive method for the determination of trace silver(1) in a basic aqueous solution.

Experimental

1 Apparatus and Reagents

A platinum wire electrode (diameter = 1. 0 mm, length = 5 mm) sealed with soft glass was used as the working electrode, the reference electrode was a saturated calomel electrode and a platinum disk (area = 20 mm^2) was used as the auxiliary electrode.

All water used in this experiment was double-distilled, first, it was distilled in a con ventional large-scale stainless steel unit, and then in a quartz distillation unit. The proce dure of preparation and purification of HDEA was described elsewhere[a]. The stock solu tion of HDEA was prepared by dissolving the purified HDEA in 0. 01 mol/L sodium hy droxide solution to give a 1. 0 × 10^{-2} mol/L HDEA solution. Other HDEA solution pre pared by dilution of the stock solution was stored in a polypropylene bottle in a nitrogen atmosphere. The 1. 0 × 10^{-2} mol/L standard silver(1) solution was prepared with silver nitrate.

2 Experimental Procedure

Prior to each measurement, the electrolysis vessel was washed with ethanol, rinsed with water. The electrodes were electrolyzed for 30 s in 0. 5 mol/L nitric acid, and then rinsed carefully with water.

To a 10 mL volumetric flask were added 0. 3 mL of 0. 5 mol/L potassium chloride. 3. 7 mL of 0. 4 mol/L potassium hydroxide, 1. 0 mL of I. 0 × 10^{-6} mol/L HDEA and an appropriate amount of silver(1) solution. The mixture solution was diluted to 10 mL with water and then transferred to the cell compartment in a dark room. During the mea surement, an automatic switch was employed to control the scan-time and to record the luminescence signal.

Results and Discussion

1 Preliminary Experiments

The electrochemiluminescence of HDEA has been studied in our laboratory[a]. The effects of 23 metal ions on the ECL of HDEA in a buffer medium of Na$_2$CO$_3$-NaHCO (pH 10. 5) were tested. The experimental results show that the ECL of HDEA is strongly catalyzed by a trace amount of silver(1), and there exists a linear relationship between the concentration of silver(1) and the luminescence intensity of HDEA.

2 Choice of Luminescence Medium

The mediums potassium sodium tartrate KOH, KCl-KOH, KOH-K$_2$SO$_4$, NaAc KOH, glycine NaCl NaOH, H$_3$BO$_3$ KOH, NaOH Na$_2$HPO$_4$, Na$_2$CO$_3$-NaHCO$_3$ and Na$_2$CO$_3$ NaHCO$_3$ NaCl were tested, under the condition of pH 10. 5, and the results show that the medium potassium chloride potassium hydroxide is the most promising one.

which HEDA could generate the brightest luminescence under the catalysis of silver(I), and the interference metal ions are comparatively few. Therefore, we chose KCl-KOH as the reacting medium.
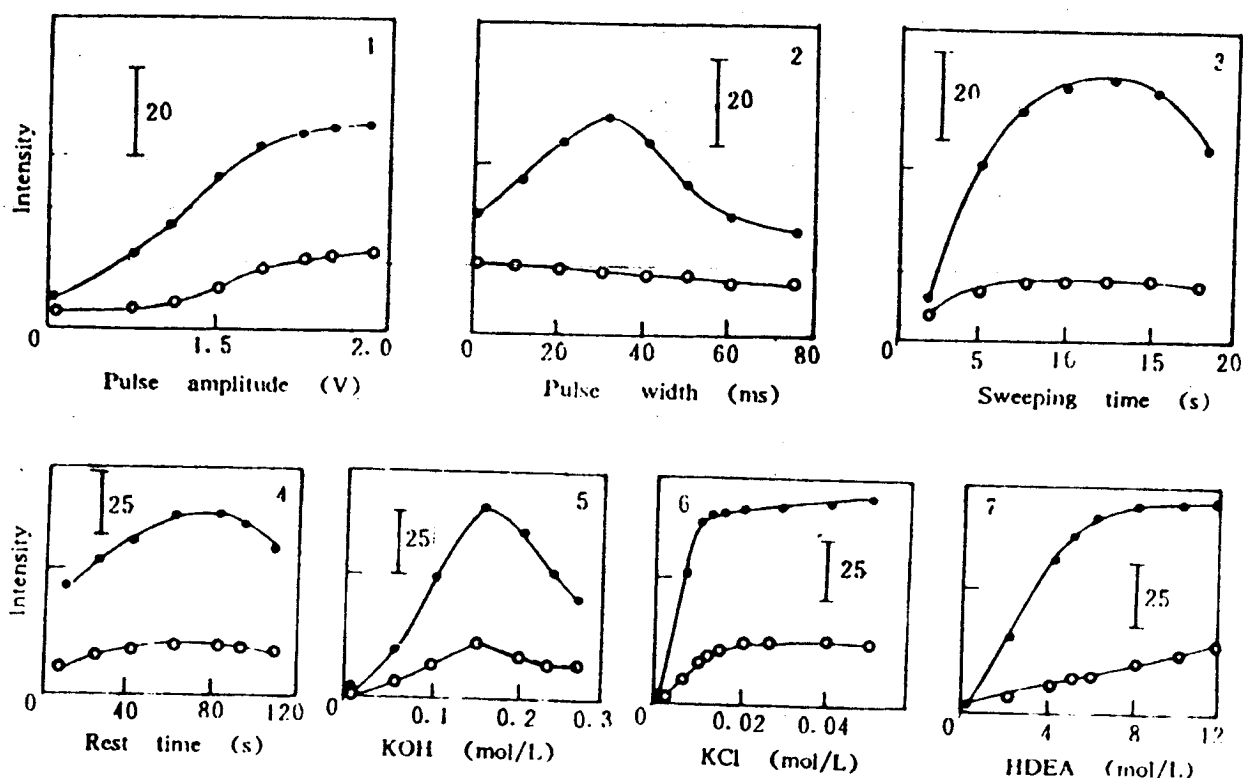

Fig. 1 Effects of variables on the luminescence intensity 5.0×10⁻⁷ mol/L silver(I) at the Pt Pt electrodes.

(1) pulse amplitude ; (2) pulse width ; (3) sweeping time ; (4) rest time ; (5) concentration of potassium hydroxide ; (6) concentration of potassium chloride ; (7) HDEA concentration. In addition to the variable under consideration, the conditions were: pulse amplse amplitude 1.6 V, pulse width 35 ms, sweeping time 10 s, rest time 1 min, 0.15 mol/L KOH, 0.02 mol/L KCl, 1.0×10⁻⁷ mol/L HDEA.

(•) without silver(I), (•) with 5.0×10⁻⁷ mol/L silver(I).

3 Chioce of Pulse Waveform

The pulse waveform effects on the electrochemiluminescence of HDEA catalyzed by silver(I) are listed in Table 1.

Table 1 Effect of pulse waveform on ECL
(5.0×10⁻⁷ mol/L silver(I), 1.0×10⁻⁷ mol/L HDEA)

Waveform(1.6 V)		Square wave	Trigonal wave	Symmetric double step wave
Intensity	a	12.8	14.5	0.8
(mV)	b	15.0	45.5	0.8

a. without silver(I), b. with 5.0×10⁻⁷ mol/L silver(I).

It is found from Table 1 that the greatest intensity is observed under the condition of trigonal wave potential, therefore, it was chosen for the following experiments.

4 Electrode Materials

Platinum-glassy carbon (Pt-C), platinum-platinum (Pt-Pt), platinum gold (Pt

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Au), silver silver (Ag-Ag), silver-platinum (Ag-Pt), platinum-copper (Pt-Cu) and glassy carbon-silver (C-Ag) as the working-auxiliary electrodes were tested. The results showed that the greatest luminescence intensity can be obtained if a platinum wire (diameter 1. 0 mm, length 5. 0 mm) and a platinum disk (area 20 mm^2) are chosen as the working electrode and auxiliary electrode, respectively.
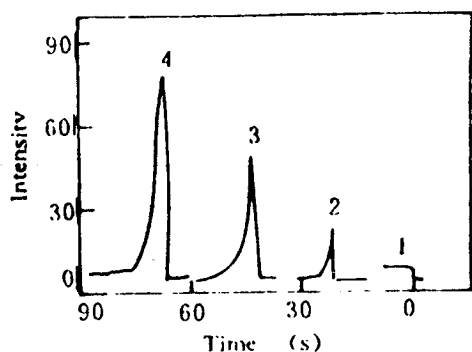

Fig. 2 Kinetic curve of HDEA electrochemiluminescence catalyzed by silver(I).

Conditions: pulse amplitude + 1. 9 V (vs. SCE), pulse width 30 ms, sweeping time 12 s, rest time 70 s, 0. 15 mol/L KOH, 0. 015 mol/L KCl and 1. 0 × 10⁻⁷ mol/L HDEA, and the temperature was controlled at 15~25 ℃.

1. without adding silver(I) and HDEA; 2. 1 + 1. 0 × 10⁻⁷ mol/L HDEA; 3. 2 + 1. 0 × 10⁻⁷ mol/L silver(I);
4. 2 + 5. 0 × 10⁻⁷ mol/L silver(I).

Fig. 3 Luminescence intensity vs. silver(I) concentration

Conditions are as those in Fig. 2.

5 Effects of Experimental Variables on the Luminescence Intensity

In order to establish the optimal conditions for the silver(I) determination, the luminescence intensity was measured as a function of trigonal-wave pulse amplitude, pulse width, sweeping and rest time, and the concentrations of potassium hydroxide, potassium · chloride and HDEA. The results of these experiments were summarized in Fig. 1. On the basis of these experiments, the kinetic curve of HDEA electrochemiluminescence catalyzed by silver(I) is presented in Fig. 2.

6 Analytical Curve, Limit of Detection and Precision

As shown in Fig. 3, the concentrations of silver(I) exhibit a good linear relationship to the luminescence intensities in the range of 5. 0 × 10⁻⁸ mol/L to 3. 0 × 10⁻⁶ mol/ L. The detection limit is 2. 0 × 10⁻⁸ mol/L for silver(I) and after 20 light intensity measurements for the solutions of 1. 0 × 10⁻⁷ mol/L silver(I) the relative standard deviation is 5%.

7 Interference by Coexited Ions

The influences of 21 metal ions and 3 anions in the ECL of HDEA in the presence of 5. 0 × 10⁻⁷ mol/L silver (I) were investigated experimentally under the above mentioned conditions previously. The results are listed in Table 2. On the basis of Table 2, nickel(II), cobalt(II), cerium(IV) and copper(II) interfere seriously with the deter
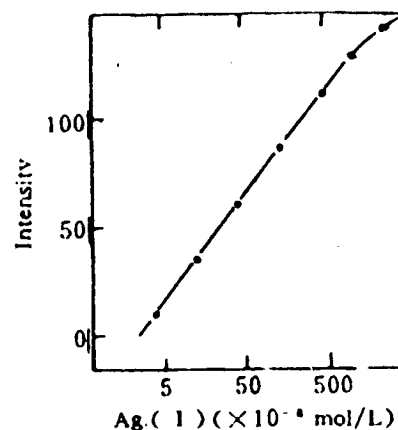
mination of 1.0×10^{-7} mol/L silver(I), while magnesium(II), lead(I), vanadium (V), lanthanum(III), calcium(II), aluminium(III), manganeses(II), zinc(II), tantalum(IV) and nitrate anion have little effect on the silver(I) determination within the metal ion to silver(I) ratio of 50 : 1, and all the other ions inhibit the electrochemiluminescence to some extent. In the presence of I^- or Br^-, the light intensity of HDEA catalyzed by silver(I) is decreased quickly, that will be discussed in a later paper.

Table 2　Effects of other ions on the electrochemiluminescence of HDEA with 1.0×10^{-7} mol/L silver(I)

Ion	Conc. (10^{-8} mol/L)	Relative Intensity	Ion	Conc. (10^{-8} mol/L)	Relative Intensity
Mg²⁺	50	100	Al(III)	30	101
Pb²⁺	100	102	Cd²⁺	20	110
Ni²⁺	0.5	104	Co(II)	0.3	72
	0.2	66		0.1	96
		~~98~~	Cr(III)	3	100
Fe(III)	20	112	Mn²⁺	5	99
Cu²⁺	0.4	91	Zn²⁺	100	107
V(V)	10	101	Au(III)	0.5	95
Sn(IV)	0.5	108	Ta(IV)	12.5	103
Tl(III)	0.5	112	Y(III)	0.5	115
La(III)	5	100	I	1.0	21
Ce(III)	0.5	54		0.2	93
	0.2	92	Br	100	57
Zr(IV)	1.0	110		0.5	91
Ca²⁺	100	97	NO₃⁻	50	104

Acknowledgement

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