Automatic Biamperometric Titration of Copper(II) by Iodide in Some Non-Aqueous Media

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Automatic biamperometric titration of copper (II) by iodide in non-aqueous media (methanol, ethanol, propanol, butanol and acetonitrile) was applied. In methanol no quantifiable curves appeared. In ethanol two end-points were observed, the first one according to the equation: $2\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI}\downarrow + \text{I}_2$ (I), while, the second according to the following equation: $\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$ (II). In propanol and butanol two end-points were observed, the first one according to the equation: $2\text{Cu}^{2+} + 2\text{I}^- \rightarrow 2\text{Cu}^+ + \text{I}_2$ (III), the second according to the following equation: $\text{Cu}^+ + \text{I}^- \rightarrow \text{CuI}\downarrow$ (IV). Finally in acetonitrile two end-points were observed, the first one according to the equation (III) and the second according to the equation (II). The proposed method was successfully applied, for the first time, for the determination of 4×10^{-5} mol L^{-1} copper (II) with RSD not more than 4.2 %. The electrochemical reversibility of $\text{Cu}^{2+}/\text{Cu}^+$ and I_2/I_3^- couples and irreversibility of Cu^+/Cu is indicated by biamperometry. The behaviour of Cu^{2+} , Cu^+ , CuI , I_2 and I_3^- has been compared. A comparison with solvents has also been made.

Key Words: Biamperometric titration, Copper(II), Iodide, Acetonitrile.

INTRODUCTION

The amperometric detection with two polarized indicating electrodes (also named as biamperometric detection) is based on the measurement and the intensity of current passing through the two identical, usually inert, electrodes, to which a small potential difference from few tens to few hundreds millivolts was applied. The current flowing in the detection cell is observed only, when solution contacting the electrodes contains two forms of reversible redox couple, it means such one for which at the same potential the oxidation of the reduced form or the reduction of oxidized form can occur. This behaviour is observed for such couples as Br_2/Br^- ; I_2/I^- ; $\text{Fe}^{3+}/\text{Fe}^{2+}$; $\text{Ce}^{4+}/\text{Ce}^{3+}$; Ag^+/Ag ; AgI/Ag , I^- ; AgBr/Ag , Br^- ; AgCl/Ag , Cl^- ; quinine/hydroquinine; $\text{Cu}^{2+}/\text{Cu}^+$ (in some non-aqueous media), etc.¹⁻³.

In biamperometric detection, in the presence of an excess of one form of reversible redox couple, the magnitude of the current measured is linearly proportional to the concentration of the second form in the solution as long as concentration over potential is not involved. When the polarizing potential difference applied to the electrodes is increased, an extension of the linear range of response is observed, however, it is associated with possible interference for other redox species present in solution. When the system detected in the solution is irreversible, the oxidation and reduction processes have activation potentials much larger, even up to 1 V. Such a large

polarizing potential difference is also applied in biamperometric detection carried out in non-aqueous solvents^{4,5}.

Potentiometric titrations of copper(II) in aqueous media were applied⁶⁻¹⁰. In these cases get a one end-point only. While in non-aqueous media some titration of Cu(II) were used as the potentiometric with Pt electrode^{11,12}, Cu electrode¹³ and ion-selective electrode¹⁴, conductometric and high frequency¹⁵; where have received some end-points as the following equations:

The reactions (1-3) get in alcohols, acetonitrile and acetone^{12,20}, while the reactions (4 and 5) get in acetone only^{13,14}.

In the present measurements, the biamperometric titration of copper(II) by iodide in alcohols and acetonitrile using Pt (two wire) indicator electrode was carried out.

EXPERIMENTAL

An automatic potentiometer and biamperometre (702 SM Titrino, Metrohm), automatic burette (806 Exchange Unit, Metrohm), indicator electrode (two polarized wire indicating electrodes) type Pt(6.0338.100), Metrohm, magnetic stirrer (728 stirrer, metrohm), sensitive balance (0.01 mg, sartorius-2474). The dilute pipette model DIP-1 (Shimadzu), having 100 mL sample syringe and five continuously adjustable pipettes

covering a volume range from 20 to 5000 μL (model Piptman P. Gilson) were used. A ultrasonic process or model POWERSONIC 405 was used to sonicate the sample solutions.

Solutions preparation: All solutions are prepared with methanol, ethanol, propanol, butanol and acetonitrile (extra pure, Merck) with analytical-reagent grade chemicals as the following: 0.01 M $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (pure, Fluka Chemika-Switzerland) was prepared by dissolving of 0.37053 g in solvent, then transferred into volumetric flask volume of 100 mL and finally complete the volume to 100 mL using same solution. 0.1 M KI was prepared by dissolving of 1.660 g in 1.0 mL deionized water, added to 60 mL of solvent, then transferred into volumetric flask volume of 100 mL and the final volume was completed to 100 mL using same solvent. All dilutions of the solutions were made with studied solvent.

The appropriate volume of the standard solution of Cu(II) is putting into volumetric flask volume of 10 mL, added studied solvent until the volume 10 mL, transferred solution to analytical cell and then titrated by iodide.

RESULTS AND DISCUSSION

Biamperometric titrations of Cu^{2+} by iodide in some non-aqueous media (methanol, ethanol, propanol, butanol and acetonitrile) were studied as the follows:

In methanol: Biamperometric titrations of Cu^{2+} by iodide in methanol did not appear quantify acceptable curves.

In ethanol: Two end-points were observed, Fig. 1, the first one according the equation:

and the second end-point according to the eqn. (3). Fig. 1 shows that, for titration 10 mL Cu^{2+} ($1 \times 10^{-3} \text{ mol L}^{-1}$), which contents 10 μmol of Cu^{2+} , gets the following: the first end-point according to titrating 10 μmol of Cu(II) with 20 μmol of added iodide to form 10 μmol of low solubility salt CuI and 5 μmol of iodine (I_2). The second end-point according to titration of formed I_2 (5 μmol) with 5 μmol of iodide to form 5 μmol of complex I_3^- .

Fig. 1. Biamperometric titration of 10 mL Cu(II) $1 \times 10^{-3} \text{ mol L}^{-1}$ by iodide 0.05 mol L^{-1} in ethanol at different volume ΔE : 1- 50 mV, 2- 100 mV, 3- 150 mV, 4- 200 mV, 5- 300 mV (Pt electrode)

In propanol: Two end-points were observed, Fig. 2, the first one according the eqn. 1 and the second end-point according to the eqn. 2. In this case did not show the end-point titration of I_2 by iodide according the eqn. 3. Fig. 2 shows that, for titration 10 mL Cu^{2+} ($1 \times 10^{-3} \text{ mol L}^{-1}$) which contents 10 μmol of Cu^{2+} , gets the following: the first end-point according to titrating 10 μmol of Cu(II) with 10 μmol of added iodide to form 10 μmol of Cu^+ and 5 μmol of iodine (I_2). The second end-point according to titration of formation Cu^+ (10 μmol) with 10 μmol of iodide to form 10 μmol of low solubility salt CuI.

Fig. 2. Biamperometric titration of 10 mL Cu(II) $1 \times 10^{-3} \text{ mol L}^{-1}$ by iodide 0.05 mol L^{-1} in propanol at different volume ΔE : 1- 50 mV, 2- 100 mV, 3- 200 mV, 4- 300 mV, 5- 400 mV, 6- 500 mV, 7- 600 mV and 8- 800 mV (Pt electrode)

In butanol: Two end-points were observed (Fig. 3, the first one according the eqn. (1) and the second end-point according to the eqn. (2). In this case did not show the end-point titration of I_2 by iodide according the eqn. (3). Fig. 3 shows that, the titration in this solvent is similar to the titration in the previous solvent (propanol), but more pronounced.

In acetonitrile: Two end-points were observed (Fig. 4), the first one according the eqn. (1) and the second end-point according to the eqn. (3). In this case the sediment CuI is not formed. Fig. 4 shows that for titration 10 mL Cu^{2+} ($1 \times 10^{-3} \text{ mol L}^{-1}$), which contents 10 μmol of Cu^{2+} , gets the following: the first end-point according to titrating 10 μmol of Cu(II) with 10 μmol of added iodide to form 10 μmol of Cu^+ and 5 μmol of iodine (I_2). The second end-point according to titration of formed iodine (5 μmol) with 5 μmol of iodide to form 5 μmol of complex I_3^- .

The optimum parameters established for automatic biamperometric titration of copper(II) by iodide in non-aqueous media (methanol, ethanol, propanol, butanol and acetonitrile) using Pt (two wire) indicator electrode were included in Table-1.

Fig. 3. Biamperometric titration of 10 mL Cu(II) $1 \times 10^{-3} \text{ mol L}^{-1}$ by iodide 0.05 mol L^{-1} ; in butanol at different volume ΔE : 1- 100 mV, 2- 200 mV, 3- 300 mV, 4- 500 mV and 5- 600 mV (Pt electrode)

Fig. 4. Biamperometric titration of 10 mL Cu(II) $1 \times 10^{-3} \text{ mol L}^{-1}$ by iodide 0.05 mol L^{-1} in acetonitrile at different volume ΔE : 1- 50 mV, 2- 100 mV, 3- 200 mV, 4- 400 mV (Pt electrode)

It is worth mentioning here that the titration of Cu^{2+} by iodide in acetonitrile is the best because of the great stability of the complex I_3^- ; where the formation constant (K_f) of I_3^- in acetonitrile is a very high compared with other studied solvents²¹⁻²⁴ ($K_f \approx 6 \times 10^6$ in acetonitrile and 2 to 9×10^4 in alcohols). The redox couple $\text{Cu}^{2+}/\text{Cu}^+$ in alcohols much high reversible compared with the redox couple I_2/I_3^- , while the exact opposite of acetonitrile. Biamperometric curves in Figs. 1-4 by using

Pt (two wire) indicated electrode showed that the redox couples $\text{Cu}^{2+}/\text{Cu}^+$ and I_2/I_3^- are reversible and the redox couple Cu^+/Cu is irreversible. The saturated diffusion constant $K = i_d/C$; where: i_d : saturated diffusion current and C concentration, mol L^{-1} , decreases as the follows: in acetonitrile, in ethanol, in propanol, in butanol.

TABLE-1
THE OPTIMUM PARAMETERS ESTABLISHED FOR
AUTOMATIC BIAMPEROMETRIC TITRATION OF COPPER(II)
BY IODIDE IN NON-AQUEOUS MEDIA (METHANOL,
ETHANOL, PROPANOL, BUTANOL AND ACETONITRILE)
USING Pt (TWO WIRE) INDICATOR ELECTRODE.

Optimum parameters	
Indicator electrode	Pt (two wire)
Non-aqueous solvents	Ethanol, propanol, butanol and acetonitrile
Temperature of solution	$30^\circ \pm 1^\circ \text{C}$
Range of concentration	$4 \times 10^{-5} - 5 \times 10^{-3} \text{ mol L}^{-1}$ in acetonitrile $1 \times 10^{-4} - 5 \times 10^{-3} \text{ mol L}^{-1}$ in alcohols
RSD	4.2 %
Better end-point	First end-point in acetonitrile and ethanol Second end-point in butanol and propanol
Volume of sample (mL)	10
Volume increment (V. step), mL	0.002-0.005
Tit. Rate (mL min^{-1})	max
Signal drift (s)	off
Equilibr. time (s)	26
Start volume (start V)	off
Filling rate (mL min^{-1})	max
Meas. impute	[U(pol)]
ΔE :	
In ethanol (mV)	100
In propanol (mV)	300
In butanol (mV)	300
In acetonitrile (mV)	100

Analytical results: Concentrations of Cu^{2+} using automatic biamperometric titration by iodide in non-aqueous media (ethanol, propanol, butanol and acetonitrile) at Pt (two wire) indicator electrode were determined. It was found that, the results were better when the first end-point is used in acetonitrile and ethanol, while in butanol and propanol the use second end-point was better than use first end-point. The proposed method was successfully applied, for the first time, to the determination of $4 \times 10^{-5} \text{ mol L}^{-1}$ copper(II) with RSD not more than 4.2 % (Table-2).

Conclusion

Automatic biamperometric titration of copper(II) by iodide in non-aqueous media (methanol, ethanol, propanol, butanol and acetonitrile) was applied. In methanol did not appear quantify acceptable curves. In ethanol two end-points were observed, the first one according to the equation: $2\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI} \downarrow + \text{I}_2$ (1), while, the second-according to the following equation: $\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$ (2). In propanol and butanol two end-points were observed, the first one according to the equation: $2\text{Cu}^{2+} + 2\text{I}^- \rightarrow 2\text{Cu}^+ + \text{I}_2$ (3) and the second-according to the following equation: $\text{Cu}^+ + \text{I}^- \rightarrow \text{CuI} \downarrow$ (4). Finally in acetonitrile two end-points were observed, the first one according to the eqn. (3) and the second according to the eqn. (2). It was found that, by using Pt electrode the redox couples $\text{Cu}^{2+}/\text{Cu}^+$ and I_2/I_3^- are reversible and the redox couple Cu^+/Cu is irreversible. The proposed method was successfully applied,

TABLE-2
AUTOMATIC BIAMPEROMETRIC TITRATION BY IODIDE IN NON-AQUEOUS MEDIA (ETHANOL,
PROPANOL, BUTANOL AND ACETONITRILE) AT Pt (TWO WIRE) INDICATOR ELECTRODE

Solvent	x_i , mmol L ⁻¹ (taken)	End- point	$\bar{X}$ *, mmol L ⁻¹ (found)	SD mmol L ⁻¹	$\frac{SD}{\sqrt{n}}$, mmol L ⁻¹	$\bar{x} \pm \frac{t \cdot SD}{\sqrt{n}}$ mmol L ⁻¹	RSD (%)
Ethanol	0.100	I	0.095	0.005	0.0022	0.095 ± 0.0061	5.0
		II	-	-	-	-	-
	0.200	I	0.198	0.010	0.0045	0.198 ± 0.012	4.8
		II	-	-	-	-	-
	0.400	I	0.401	0.018	0.0080	0.401 ± 0.022	4.6
		II	-	-	-	-	-
	0.600	I	0.602	0.026	0.012	0.602 ± 0.033	4.4
		II	-	-	-	-	-
	0.800	I	0.802	0.038	0.017	0.802 ± 0.047	4.2
		II	0.791	0.027	0.012	0.791 ± 0.033	4.8
	1.00	I	1.00	0.039	0.017	1.00 ± 0.048	3.9
		II	0.99	0.046	0.021	0.99 ± 0.057	4.6
	2.00	I	1.99	0.078	0.035	1.99 ± 0.097	3.7
		II	1.97	0.088	0.039	1.97 ± 0.109	4.4
	3.00	I	3.02	0.105	0.047	3.02 ± 0.130	3.5
		II	2.99	0.132	0.059	2.99 ± 0.164	4.4
	4.00	I	4.05	0.14	0.063	4.05 ± 0.174	3.6
		II	3.96	0.18	0.080	3.96 ± 0.223	4.6
Propanol	0.100	I	-	-	-	-	-
		II	0.096	0.004	0.0018	0.096 ± 0.005	3.8
	0.200	I	-	-	-	-	-
		II	0.198	0.008	0.0036	0.198 ± 0.01	3.8
	0.400	I	-	-	-	-	-
		II	0.401	0.015	0.007	0.401 ± 0.019	3.7
	0.600	I	0.592	0.029	0.013	0.592 ± 0.036	4.9
		II	0.600	0.022	0.01	0.600 ± 0.028	3.6
	0.800	I	0.790	0.038	0.017	0.790 ± 0.047	4.8
		II	0.803	0.027	0.012	0.803 ± 0.033	3.4
	1.00	I	0.994	0.046	0.020	0.994 ± 0.055	4.6
		II	1.01	0.031	0.014	1.01 ± 0.039	3.1
	2.00	I	1.99	0.088	0.039	1.99 ± 0.110	4.4
		II	2.00	0.056	0.025	2.00 ± 0.069	2.8
	3.00	I	2.98	0.131	0.059	2.98 ± 0.162	4.4
		II	3.01	0.080	0.036	3.01 ± 0.101	2.7
	4.00	I	3.97	0.18	0.080	3.97 ± 0.222	4.5
		II	4.02	0.11	0.049	4.02 ± 0.136	2.8
Butanol	0.080	I	-	-	-	-	-
		II	0.078	0.0035	0.0016	0.078 ± 0.0044	4.5
	0.100	I	-	-	-	-	-
		II	0.098	0.0033	0.0015	0.098 ± 0.0042	3.4
	0.200	I	-	-	-	-	-
		II	0.201	0.007	0.0031	0.201 ± 0.0086	3.3
	0.400	I	0.386	0.018	0.0080	0.386 ± 0.022	4.8
		II	0.404	0.013	0.0058	0.404 ± 0.016	3.2
	0.600	I	0.597	0.027	0.012	0.597 ± 0.033	4.6
		II	0.602	0.019	0.0085	0.602 ± 0.023	3.2
	0.800	I	0.793	0.036	0.016	0.793 ± 0.045	4.5
		II	0.801	0.025	0.011	0.801 ± 0.030	3.1
	1.00	I	0.997	0.043	0.019	0.997 ± 0.053	4.3
		II	1.02	0.029	0.013	1.02 ± 0.036	2.9
	2.00	I	1.99	0.085	0.038	1.99 ± 0.105	4.3
		II	2.02	0.054	0.024	2.02 ± 0.067	2.7
	3.00	I	2.99	0.129	0.057	2.99 ± 0.160	4.3
		II	3.02	0.079	0.035	3.02 ± 0.097	2.6
	4.00	I	3.98	0.18	0.080	3.98 ± 0.222	4.4

Solvent	x_i , mmol L ⁻¹ (taken)	End- point	$\bar{X}$ *, mmol L ⁻¹ (found)	SD mmol L ⁻¹	$\frac{SD}{\sqrt{n}}$, mmol L ⁻¹	$\bar{x} \pm \frac{t \cdot SD}{\sqrt{n}}$ mmol L ⁻¹	RSD (%)
Acetonitrile	5.00	II	4.00	0.11	0.049	4.00 ± 0.136	2.7
		I	4.99	0.22	0.098	4.99 ± 0.272	4.5
		II	5.01	0.14	0.063	5.01 ± 0.174	2.9
	0.040	I	0.039	0.0017	0.0008	0.039 ± 0.0022	4.2
	0.050	II	0.040	0.0018	0.0008	0.040 ± 0.0022	4.5
		I	0.050	0.0019	0.0008	0.050 ± 0.0022	3.8
	0.060	II	0.049	0.0021	0.0009	0.049 ± 0.0025	4.2
		I	0.062	0.0021	0.0009	0.062 ± 0.0025	3.4
	0.080	II	0.058	0.0024	0.0011	0.058 ± 0.0030	4.1
		I	0.081	0.0028	0.0012	0.081 ± 0.0033	3.2
	0.100	II	0.079	0.0032	0.0014	0.079 ± 0.0040	4.0
		I	0.099	0.0030	0.0013	0.099 ± 0.0036	3.1
	0.200	II	0.098	0.004	0.0018	0.098 ± 0.0050	3.9
		I	0.200	0.006	0.0027	0.200 ± 0.0075	3.0
	0.400	II	0.193	0.008	0.0036	0.193 ± 0.010	3.8
		I	0.402	0.011	0.0049	0.402 ± 0.014	2.8
	0.600	II	0.397	0.015	0.0067	0.397 ± 0.018	3.7
		I	0.603	0.016	0.0071	0.603 ± 0.02	2.7
	0.800	II	0.595	0.021	0.0094	0.595 ± 0.026	3.5
		I	0.800	0.020	0.0089	0.800 ± 0.025	2.5
	1.00	II	0.799	0.026	0.012	0.799 ± 0.033	3.2
		I	1.00	0.024	0.011	1.00 ± 0.030	2.4
	2.00	II	1.00	0.029	0.013	1.00 ± 0.036	2.9
		I	2.01	0.048	0.021	2.01 ± 0.058	2.4
	3.00	II	1.99	0.048	0.021	1.99 ± 0.058	2.4
		I	3.00	0.072	0.032	3.00 ± 0.089	2.4
	4.00	II	3.00	0.075	0.034	3.00 ± 0.093	2.5
		I	4.00	0.10	0.045	4.00 ± 0.125	2.5
	5.00	II	3.97	0.10	0.045	3.97 ± 0.125	2.6
		I	5.02	0.13	0.058	5.02 ± 0.161	2.6
		II	4.98	0.14	0.063	4.98 ± 0.175	2.8

*n = 5, t = 2.776, I- using first end-point, II- using second end-point.

for the determination of 4×10^{-5} mol L⁻¹ copper(II) with RSD not more than 4.2 %.

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