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APPLICABILITY OF GLASSY CARBON – PLATINUM ELECTRODE SYSTEM FOR BIAMPEROMETRIC INDICATION IN ACETONITRILE MEDIUM USING COPPER (II)–COPPER (I) COUPLE: ESTIMATION OF ORGANOTRITHIOCARBONATES AND THIOUREAS

DEBASHISH GHOSH* **and NAVEEN RAGHUBANSHI**

Department of Chemistry, Harish Chandra Post Graduate College,
VARANASI – 221001 (U.P.) INDIA

ABSTRACT

Applicability of glassy carbon-platinum electrode system has been examined for biamperometric indication in acetonitrile medium utilizing the presence of Cu (II)–Cu (I) couple. Postassium butyl, isobutyl, benzyl and dodecyl trithiocarbonates have been estimated using copper (II) perchlorate in the first series of experiments and in the second one, copper (II) nitrate has been used as oxidant for the determination of thiourea and some of its derivatives. Cu (II)–Cu (I) reversible couple being generated just on the completion of the test substances, reversed L-shaped titration curves, with remarkably sharp breaks, have been obtained leading to precise and accurate results (error not exceeding ± 1.07%) even for determinations in low concentration range.

Key words: Glassy carbon-platinum electrode system, Biamperometric indication, Acetonitrile, Cu (II)–Cu (I) couple.

INTRODUCTION

Among the non-aqueous solvents, acetonitrile by virtue of being resistant to oxidation or reduction and possessing high dielectric constant has been found to be a convenient medium for oxidimetric estimations.

Copper (II) as an oxidant, in aqueous medium, could not gain much importance because of its limited oxidizing capacity and susceptibility of its reduced species i.e., Cu (I) to aerial oxidation. It is only after the recognition of the stabilization of copper (I) in acetonitrile, that copper (II) has emerged as an excellent oxidant[1,2] (possessing high redox

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[*] Author for correspondence; E-mail: debashish.ghosh25@gmail.com; Mo.: +91 9450245631

potential coupled with suitable stability) for analytical purposes. Thus, Kratochvil et al.,[3-6] used both hydrated and anhydrous copper (II) perchlorate for the oxidative determination of tetrabutyl ammonium iodide, thiourea, aryl amines and ferrorcenes in acetonitrile by potentiometric titration using a platinum wire indicator electrode and a silver – 0.01 M silver nitrate (in acetonitrile) reference electrode. Mruthyunjaya and Murthy[7,8] have employed copper (II) perchlorate as well as copper (II) nitrate for determinations of potassium ethyl xanthate, thiourea and iodides of Cu (I), Na and K in which end point was registered potentiometrically using a glass and platinum electrode assembly. These authors have also reported that the oxidizing power of copper (II) in acetonitrile is much influenced by the anion associated with it. Verma and Kumar[9-12] have also reported the estimation of xanthates, phenyl hydrazides, mercaptopyrimidines, ascorbic acid and several other organic compounds using either copper (II) perchlorate or copper (II) nitrate as oxidant. In these estimations, the end points have been judged either visually using diphenylamine/diphenyl benzidine as indicator[9] or potentiometri-cally using platinum as indicator electrode and modified calomel (saturated methanolic potassium chloride solution)/antimony as reference electrode.

Glassy carbon electrode[13-20], in recent years, has successfully been applied in various electroanalytical techniques and also in other electrometric measurements both in aqueous and non-aqueous media. The present communication reports the application of glassy carbon electrode in combination with platinum for biamperometric indication in the estimation of organotrithiocarbonates in acetonitrile medium using copper (II) perchlorate as oxidant. In order to ascertain the general applicability of the technique for non-aqueous estimations involving Cu (II)–Cu (I) reversible current indicating couple, some thioureas have also been estimated in the same solvent using another copper (II) salt i.e., copper (II) nitrate.

Both organotrithiocarbonates and thioureas are important class of organosulphur compounds having useful applications in the field of analysis, industry and medicine. Since many compounds of this class are insoluble in aqueous medium, non-aqueous estimation of these compounds using a simple and reliable technique is of considerable interest.

EXPERIMENTAL

Electrode system

The electrode system, used in the present studies, consisted of a glassy carbon and a micro-platinum electrode fitted tightly in a rubber disc (at a fixed interspace ~ 3 cm) provided with holes for the insertion of burette tip and for the inlet of nitrogen or carbon dioxide gas. The rest of the apparatus along with its circuitry arrangement was essentially the same as adopted in the conventional biamperometric technique. The glassy carbon electrode, before use, was carefully hand-polished with alumina-water paste using polishing cloth and then rinsed with double distilled water and finally with methanol. Likewise, the platinum electrode was cleaned by dipping in chromic-sulphuric acid mixture for five minutes followed by thorough wash with distilled water and subsequently rinsed with methanol.

Reagents

All reagents used were of guaranteed quality.

Acetonitrile was distilled twice over P_2O_5 (5 g/L) before use.

Solid copper (II) perchlorate (hydrated) was prepared following the recommended method[5] which consisted of adding a slight excess of perchloric acid (60%) to a suspension of copper (II) carbonate in water and subsequent removal of carbon dioxide by boiling. The blue crystalline compound obtained on cooling was separated and dried. Its stock solution was prepared by dissolving weighed quantity in acetonitrile and standardized[10] iodometrically in aqueous acidic medium.

The stock solution of copper (II) nitrate was prepared by dissolving weighed quantity of its commercial sample in acetonitrile; it was standardized using EDTA[21] in aqueous medium.

The organotrithiocarbonates (potassium butyl-, isobutyl-, benzyl- and dodecyl-) were prepared following recommended[22] procedure which consisted of shaking an equimolar mixture of corresponding mercaptan, potassium hydroxide and carbon disulphide at a temperature below 10^oC. The resulting product was purified by recrystallisation from suitable solvent mixtures and kept in a desiccator over phosphorous pentoxide; its purity was checked using iodinesolution[23].

Commercial samples of thiourea and its derivatives (phenyl-, biphenyl- and allyl-) were recrystallised and purity checked using Ce (IV) [24].

Method

Determination of organotrithiocarbonates using copper (II) perchlorate

An aliquot of the solution of organotrithiocarbonate in acetonitrile containing known amount of the compound was taken in the titration cell and diluted (using the same solvent) to a total titration volume of 30 mL. The glassy carbon-platinum electrode assembly was then immersed into the test solution and a fixed polarizing emf (varied in the range of

200-300 mV), obtained from a battery operated potential divider, was impressed between the electrodes keeping glassy carbon as the positive. Standard copper (II) perchlorate (0.01 – 0.04 N) was added from a semimicro burette (provided with a guard tube containing silica gel to protect the titrant from atmospheric moisture) and the current passing through the cell was measured with a sensitive galvanometer (after lapse of usually two minutes) following each addition of the titrant. The contents of the cell was kept stirred uniformly throughout the titration, using a magnetic stirrer actuated by stabilized A.C. supply. The equivalence point of each titration was obtained from the plot of cell current (as indicated by galvanometer deflection) and the volume of the titrant added.

Determination of thioureas using copper (II) nitrate

Thioureas were determined in the same way as described above (for organotrithiocarbonates) using now copper (II) nitrate solution (0.0122-0.0548 N) as titrant at a definite emf varied in the range of 100-200 mV.

Results for determinations of organotrithiocarbonates and thioureas are presented in Table 1. Four representative titration curves, two each for organotrithiocarbonates (at 200 and 300 mV) and thioureas (at 100 and 200 mV) are shown in Fig. 1 for illustrating the general nature of titration curves and the effect of applied polarizing emf.

Table 1: Glassy carbon-platinum biamperometric determination of organotrithiocarbonates and thioureas in acetonitrile medium Oxidant: Copper (II) perchlorate

Substance estimated	Approximate molarity	Amount of substance (mg)		Error %
		Taken	Found	
Potassium butyl trithiocarbonate	4.89×10^{-4}	3.004	3.025	+0.69
	1.71×10^{-3}	10.514	10.465	-0.46
	4.16×10^{-3}	25.534	25.675	+0.55
	4.89×10^{-3}	30.040	29.927	-0.37
Postassium isobutyl trithiocarbonate	4.81×10^{-4}	2.952	2.963	+0.37
	1.92×10^{-3}	11.808	11.773	-0.29
	2.88×10^{-3}	17.712	17.823	+ 0.62
	4.81×10^{-3}	29.520	29.682	+0.54

Cont…

Substance estimated	Approximate molarity	Amount of substance (mg)		Error %
		Taken	Found	
Postassium benzyl trithiocarbonate	4.66×10^{-4}	3.336	3.361	+0.74
	1.63×10^{-3}	11.676	11.729	+0.45
	3.26×10^{-3}	23.352	23.506	+0.65
	4.19×10^{-3}	30.024	30.136	+0.37
Potassium dodecyl trithiocarbonate	2.39×10^{-4}	2.272	2.279	+0.30
	1.19×10^{-3}	11.360	11.302	-0.51
	1.91×10^{-3}	18.176	18.109	-0.36
	2.87×10^{-3}	27.264	27.417	+0.56
Oxidant : Copper (II) nitrate				
Thiourea	9.05×10^{-4}	2.068	2.056	-0.58
	2.26×10^{-3}	5.170	5.136	-0.65
	4.98×10^{-3}	11.374	11.319	-0.48
	6.79×10^{-3}	15.510	15.580	+0.45
Phenyl thiourea	7.30×10^{-4}	3.336	3.366	+0.89
	1.82×10^{-3}	8.340	8.387	+0.56
	4.38×10^{-3}	20.016	20.093	+0.38
	5.47×10^{-3}	25.020	25.192	+0.68
Biphenyl thiourea	5.72×10^{-4}	3.924	3.882	-1.07
	1.71×10^{-3}	11.772	11.827	+0.46
	3.15×10^{-3}	21.582	21.473	-0.50
	3.72×10^{-3}	25.506	25.611	+0.41
Allyl thiourea	7.09×10^{-4}	2.472	2.453	-0.76
	2.83×10^{-3}	9.888	9.844	-0.44
	3.90×10^{-3}	13.596	13.674	+0.57
	5.31×10^{-3}	18.540	18.497	-0.23

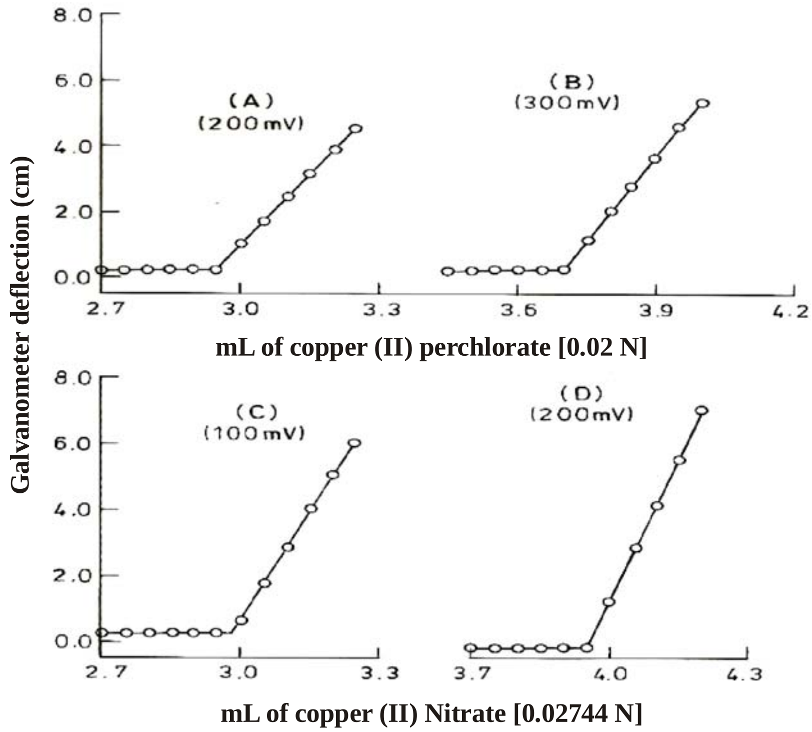
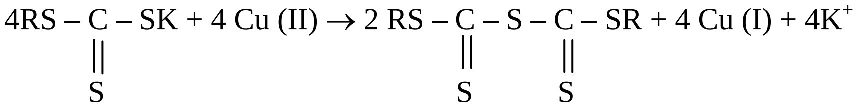


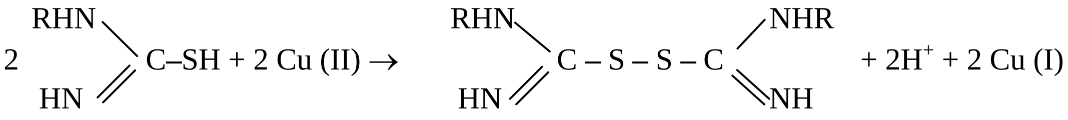
Fig. 1: Current-volume plots in the glassy carbon-platinum biamperometric indication of potassium butyl trithiocarbonate [(A) 12.016 mg, (B) 15.020 mg] and Thiourea [(C) 6.204 mg, (D) 8.272 mg] in acetonitrile

RESULTS AND DISCUSSION

The present estimations are based on the oxidation of organotrithiocarbonates and thioureas by copper (II) perchlorate and copper (II) nitrate, respectively as given below :



$$4RS-\underset{\underset{S}{\|}}{C}-SK + 4\,Cu\,(II) \rightarrow 2\,RS-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{S}{\|}}{C}-SR + 4\,Cu\,(I) + 4K^+$$



Cu (I) formed as a result of oxidation of the test compounds remains stabilized by forming the complex ion $[Cu\ (CH_3CN)_4]^+$ with the medium i.e., acetonitrile. This stabilization of Cu (I) in acetonitrile has two advantages. Firstly, it helps in avoiding error arising out of possible aerial oxidation of Cu (I) allowing the titration to be performed even without arranging for inert atmosphere and secondly it facilitates in producing reliable current indicating Cu (II)–Cu (I) couple needed for biamperometric indication. The titration curves obtained, in general, are of reversed L-shape. This is anticipated because in the pre-equivalence region of the titration only the reduced form i.e., Cu (I) (stabilized in acetonitrile) is available. On completion of the oxidation process, any additional oxidant added introduces free (unconsumed) Cu (II) resulting in the formation of Cu (II)–Cu (I) couple. This causes sudden rise of cell current which goes on increasing, proportionately, with the progressive addition of the titrant. The breaks in the titration curves, indicative of equivalence point, are remarkably sharp and reproducible. Further, for estimation with a particular concentration of titrant under uniform stirring condition, an increase in emf within prescribed range, does not affect either the general nature of the titration curve or the location of end point; it simply increases the current value in the post-equivalence region (Fig. 1). It is to be noted that although the current-volume plots as obtained here, bear similarity to those reported with the conventional biamperometric titrations using two identical platinum electrodes[25], the present dissimilar electrode combination has been found to be helpful in getting very sharp breaks facilitating a clear-cut location of end point.

The results obtained (Table 1) both for organotrithiocarbonates (2-30 mg) and thioureas (2-25 mg) are accurate and precise (reproducibility checked by a number of experiments) with percentage error varying in the narrow range of – 1.07 to + 0.89.

It is concluded therefore, that the glassy carbon–platinum biamperometry, which is simple and avoids much of instrumental farbrication, can successfully be applied for determinations in acetonitrile medium using copper (II) as oxidant.

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