



Biamperometric Indication with Glassy Carbon-Platinum Electrode System in Non-Aqueous Media Using Iodine-Iodide Couple: Determination of Xanthates and Dithiocarbamates

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(Received: 7 June 2011;

Accepted: 21 December 2011)

AJC-10882

Glassy carbon-platinum electrode combination has been applied for biamperometric indication in non-aqueous media using iodine-iodide couple for current indication. In the first series of experiments, carried out in acetonitrile medium, potassium alkyl xanthates have been determined using N-bromosuccinimide as the oxidant in the presence of potassium iodide and in the second series metal diethyl dithiocarbamates have been estimated in N,N-dimethylformamide using iodine monobromide. Reverse L-shaped titration curves with well-defined and reproducible breaks leading to precise results have been obtained both for xanthates (3.27-36.04 mg) and diethyl dithiocarbamates (5.07-38.82 mg) with errors not exceeding $\pm 1\%$.

Key Words: Xanthates, Dithiocarbamates, Iodine-iodine coupling, Glass carbon electrode.

INTRODUCTION

Glassy carbon electrode has successfully been applied¹⁻¹⁰ in recent years, for various electrometric determinations and for other electroanalytical studies. Its combination with a platinum electrode has also been found to be suitable for biamperometric indication in aqueous medium¹¹. An attempt has now been made to explore the suitability of this electrode combination for biamperometric indication in purely non-aqueous media. The present communication reports the redox determination of small amounts of (i) potassium ethyl-, propyl-, butyl- and amyl xanthates using N-bromosuccinimide in acetonitrile medium in the presence of potassium iodide and (ii) diethyl dithiocarbamates of cadmium, lead, zinc and mercury using iodine monobromide in N,N-dimethyl formamide medium.

Both xanthates and dithiocarbamates constitute an important class of sulphur compounds having various applications in medicine, agriculture and industry. Further, many of these compounds are insoluble in water and also the soluble ones have the tendency to get decomposed in acidic or alkaline solutions which generally serves as the medium for a variety of redox determinations in aqueous medium. As such, therefore, the estimation of these compounds in non-aqueous medium, applying simple and reliable technique, is of considerable importance.

EXPERIMENTAL

Electrode system: The electrode system consisted of a glassy carbon electrode and a micro platinum electrode fitted suitably (interspace *ca.* 3 cm) in a rubber disc having necessary holes for burette tip and for supply of nitrogen gas. The circuit arrangement was essentially the same as is adopted in conventional biamperometric titrations.

Acetonitrile (IDPL) was distilled twice over P_2O_5 (5 g/L). N,N-Dimethyl formamide (E. Merck) was first kept in contact with sodium carbonate for 48 h (with occasional shakings) and the decanted liquid was distilled. The fraction boiling in the range of 148.5-149.5 °C was collected and stored in a well stoppered bottle.

The sample of N-bromosuccinimide (BDH) was recrystallized from minimum amount of hot water and dried first on a porous pot and then in a vacuum desiccator. Its solution of desired strength in acetonitrile was prepared using weighed quantity (a little more than calculated) and standardized iodometrically¹² in aqueous medium.

Iodine monobromide was prepared and purified following the method suggested by Popov and Skelly¹³. Its stock solution was prepared by dissolving a weighed quantity (a little more than calculated) and was standardized iodometrically¹⁴ in aqueous medium and stored in the dark.

The compounds undertaken for estimation *i.e.*, potassium alkyl xanthates and metal diethyl dithiocarbamates, as

mentioned earlier, were prepared and purified following recommended methods¹⁵⁻¹⁷.

Method

Determination of xanthates in acetonitrile medium:

An aliquot of the solution of xanthate in acetonitrile, containing known amount of the compound, was taken in the titration cell and mixed with 5 mL of 1 % potassium iodide solution prepared in the same solvent. Adequate amount of acetonitrile was added to make its volume 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 250-350 mV) obtained from a battery operated potential divider, was applied with glassy carbon as the positive electrode. The titrant N-bromosuccinimide solution (0.0125-0.025 M) also prepared in acetonitrile, was added from a semi-micro burette and the cell current was measured (usually after a lapse of 2 min) following each addition using a sensitive galvanometer. The solution was kept stirred uniformly during titration using a magnetic stirrer actuated by stabilized A.C. supply. The equivalence point was obtained, as usual, from the corresponding plots of galvanometer deflection *versus* volume of the titrant added.

Determination of diethyl dithiocarbamates in N,N-dimethyl formamide (DMF) medium: A known amount of test solution of metal diethyl dithiocarbamate in DMF was taken in the titration cell and was diluted to 30 mL with DMF. Standard solution of iodine monobromide (0.0125-0.025 M) was added from a semi-microburette and the biamperometric estimation (with glassy carbon-platinum electrode system) was carried at a constant polarising emf varied in the range of 200-300 mV.

The results of estimation for xanthates and diethyl dithiocarbamates are presented in Table-1 (A and B). In order to illustrate the actual nature of titration curves and the effect of variation of emf thereon, two representative current-volume plots for potassium ethyl xanthate at two different emf values (250 and 350 mV) and also of cadmium diethyl dithiocarbamate at 200 and 300 mV are shown in Fig. 1.

RESULTS AND DISCUSSION

The determinations reported here are based on the oxidation of potassium alkyl xanthates by N-bromosuccinimide in the presence of potassium iodide and that of metal diethyl dithiocarbamates by iodine monobromide in DMF producing dixanthogens and thiuram disulphides, respectively.

TABLE-1
GLASSY CARBON-PLATINUM BIAMPEROMETRIC DETERMINATION OF XANTHATES AND
DIETHYL DITHIOCARBAMATES IN NON-AQUEOUS MEDIA

(A) Medium: Acetonitrile		Oxidant: N-Bromosuccinimide		
Substance estimated	Approximate molarity	Amount of substance (mg)		Error (%)
		Taken	Found	
Potassium ethyl xanthate	7.40×10^{-4}	3.590	3.605	+ 0.41
	2.09×10^{-3}	10.052	10.136	+ 0.83
	4.18×10^{-3}	20.104	19.952	- 0.75
	6.86×10^{-3}	33.028	33.253	+ 0.68
Potassium propyl xanthate	7.06×10^{-4}	3.695	3.659	- 0.97
	2.26×10^{-3}	11.824	11.761	- 0.53
	5.08×10^{-3}	26.604	26.748	+ 0.54
	6.50×10^{-3}	33.994	33.806	- 0.55
Potassium butyl xanthate	6.94×10^{-4}	3.920	3.953	+ 0.84
	1.94×10^{-3}	10.976	11.061	+ 0.77
	4.71×10^{-3}	26.656	26.735	+ 0.29
	6.38×10^{-3}	36.064	36.243	+ 0.49
Potassium amyl xanthate	5.39×10^{-4}	3.272	3.287	+ 0.45
	1.34×10^{-3}	8.180	8.242	+ 0.75
	3.23×10^{-3}	19.632	19.520	- 0.57
	5.39×10^{-3}	32.720	32.567	- 0.46
(B) Medium: N,N-Dimethylformamide		Oxidant: Iodine monobromide		
Cadmium diethyl dithiocarbamate	4.39×10^{-4}	5.392	5.416	+ 0.44
	1.09×10^{-3}	13.480	13.377	- 0.76
	1.86×10^{-3}	22.916	22.993	+ 0.33
	3.07×10^{-3}	37.744	37.811	+ 0.17
Lead diethyl dithiocarbamate	3.59×10^{-4}	5.424	5.472	+ 0.88
	7.18×10^{-4}	10.848	10.889	+ 0.37
	1.16×10^{-3}	17.628	17.498	- 0.73
	2.24×10^{-3}	33.900	33.739	- 0.47
Zinc diethyl dithiocarbamate	4.67×10^{-4}	5.072	5.110	+ 0.74
	1.16×10^{-3}	12.680	12.752	+ 0.56
	1.86×10^{-3}	20.288	20.167	- 0.59
	3.50×10^{-3}	38.040	38.163	+ 0.32
Mercury diethyl dithiocarbamate	3.47×10^{-4}	5.176	5.218	+ 0.81
	7.81×10^{-4}	11.646	11.554	- 0.78
	1.73×10^{-3}	25.880	25.817	- 0.24
	2.60×10^{-3}	38.820	38.760	- 0.16

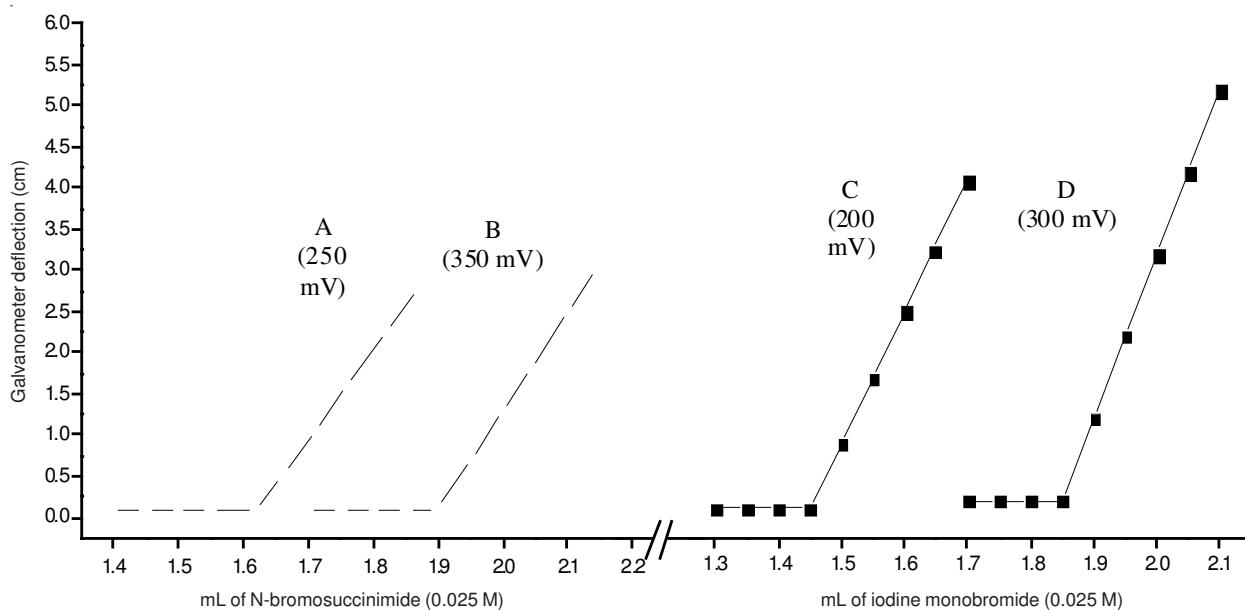
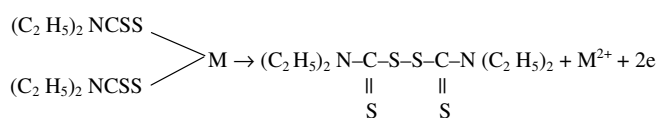
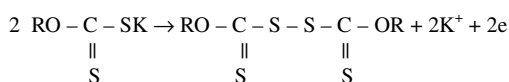


Fig. 1. Glassy carbon-platinum biamperometric determination of potassium ethyl xanthate in acetonitrile (A) 12.924 mg (B) 14.360 mg and cadmium diethyl dithiocarbamate in DMF (C) 14.828 mg (D) 18.872 mg



Both the reactions are fast and quantitative facilitating direct determination^{12,18,19}. On completion of oxidation of xanthates by N-bromosuccinimide, in the presence of potassium iodide and that of dithiocarbamates by iodine monobromide in the respective non-aqueous media, any additional amount of corresponding oxidant added generates iodine which causes the inception of the iodine-iodide couple. As the presence of this reversible couple in solution is responsible for the sudden onset of cell-current, which increases proportionately with the progressive addition of the oxidant, the current-volume plots, as anticipated, are uniformly of reversed L-shape both for the determinations of xanthates and dithiocarbamates. Application of a higher polarizing emf (200-350 mV) does not affect either the general nature of titration curve or the location of end point; it simply enhances the cell-current in the post equivalence region. Although the current-volume curves as obtained here, show similarity to those reported with the conventional biamperometric titrations employing two identical platinum electrodes²⁰, the dissimilarity of the present electrode system has been found to offer an additional advantage of yielding very sharp breaks thus facilitating unambiguous location of end point.

The results obtained [Table-1 (A) and (B)] for determinations of potassium alkyl xanthates (3.27- 36.04 mg) in acetonitrile and that for metal diethyl dithiocarbamates (5.07-

38.82 mg) in DMF are accurate and reproducible (as confirmed by repeated experiments) with errors remaining restricted to $\pm 1\%$.

Thus the sharp breaks in titration curves yielding precise and accurate results amply justifies the suitability of the present glassy carbon-platinum electrode system for biamperometric indication in non-aqueous media utilizing iodine-iodide reversible couple.

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