Indian Journal of Chemistry
Vol. 46A, July. 2007, pp. 1121-1124

A pulse polarographic method for the analysis of zinc dithiocarbamates

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Received 6 December 2006; revised 30 April 2007

An extremely sensitive pulse polarographic method for the determination of zinc dimethyldithiocarbamate (an agricultural fungicide) and zinc di-*n*-pentyldithiocarbamate (a petroleum additive), has been developed based on the reaction of their dithiocarbamate moiety with copper(II) perchlorate in acetonitrile medium. Well defined diffusion-controlled peaks are observed at –140 mV and –130 mV (vs SCE) for zinc dimethyldithiocarbamate and zinc di-*n*-pentyldithiocarbamate respectively. The peaks shows approximately four-fold higher sensitivity than that obtained by pulse polarography of the zinc dithiocarbamate alone. A linear relationship is obtained between concentration of the zinc dithiocarbamate [added to copper(II)] and peak current. Using cyclic voltammetry, a probable mechanism for the zinc dithiocarbamate-copper(II) reaction has been proposed.

IPC Code: G01N27/00

Among the metal dithiocarbamates, zinc dialkyldithiocarbamates [$Zn(dtc)_2$] form a distinct class. These compounds, especially those derived from relatively simple dialkylamines, have attained special importance among synthetic fungicides and petroleum additives[1]. Zinc dimethyldithiocarbamate (ziram) is a commercial fungicide and zinc di-*n*-pentyldithiocarbamate (vanlube AZ) is a petroleum additive commonly used to improve the quality of fuel. In view of the wide commercial importance of zinc dithiocarbamates, a variety of methods have been reported for their determination[2-5]. The commonly employed approach, however, involves decomposing each dithiocarbamate with hot mineral acids and determination of the corresponding amine and carbon disulphide. Usually carbon disulphide is selected and measured colorimetrically as copper dithiocarbamate complex[1].

$$Zn(R_2N.CS.S)_2 + 2H^+ \longrightarrow 2R_2NH + 2\,CS_2 + Zn^{2+}$$

Derivative spectrophotometric and gas chromatographic techniques have also been employed to measure carbon disulphide (as dithiocarbamates)[6,7]. The method is, however, tedious, time-consuming and requires not only a special apparatus but careful control of experimental conditions for ensuring quantitative evolution of carbon disulphide. This, therefore, creates a need for a method which besides being accurate and precise, should also be rapid.

Pulse polarography has emerged as a reliable and sensitive tool for trace analysis. The present paper describes its application to analysis of the commercially important compounds, zinc dithiocarbamates [($Zn(dtc)_2$)], by making use of their reaction with copper(II) perchlorate in acetonitrile. Copper(II) perchlorate (in acetonitrile) gives a well-defined diffusion controlled peak at –300 mV, while zinc dimethyldithiocarbamate, [$Zn(dmdtc)_2$] and zinc di-*n*-pentyldithiocarbamate [$Zn(dpdtc)_2$] give similar peaks at 240 and 225 mV respectively. However, when [$Zn(dmdtc)_2$] or [$Zn(dpdtc)_2$] (in acetonitrile) is added to copper(II) perchlorate, there is decrease in current intensities of the peaks due to copper(II) and both the dithiocarbamates, with two new peaks appearing simultaneously at –140 mV and –130 mV. The above trend continues till copper(II):$Zn(dtc)_2$ molar ratio of 2:1 is achieved. At this point, the peaks due to copper(II) as well as the dithiocarbamates disappear completely and the new peaks attain their full current intensities. It is extremely important to mention here that current intensity of the new peaks is approximately four times higher than that of the corresponding peak obtained with either of above $Zn(dtc)_2$ alone. This remarkable sensitivity of the new peaks coupled with linear relationship obtained between concentration of each $Zn(dtc)_2$ added to copper(II) and current intensity of each peak is the basis of the proposed differential pulse polarographic method. The method has also been applied to other $Zn(dtc)_2$ prepared in the laboratory to test its utility in formulated products based on zinc dithiocarbamates.

Experimental

Acetonitrile (Merck) was kept over phosphorus pentoxide (5 g l^{-1}) and distilled twice. Tetraethylammonium perchlorate (TEAP) was

prepared by earlier reported method[8]. Its standard solution was prepared by dissolving 2.296 g of pure compound in one litre of acetonitrile. Zinc dimethyldithiocarbamate, (Ziram, Fluka, Switzerland) was recrystallized before use. Zinc diethyl-, di-*n*-propyl-, di-*n*-butyl- and di-*n*-pentyl dithiocarbamates were prepared by adding dropwise with constant stirring a solution of zinc sulphate in less than stoichiometric amounts to an aqueous solution of the respective sodium dialkyldithiocarbamate. The products were removed by filtration and dried in vacuum. The purity of each compound was checked by known methods[1]. Hydrated copper(II) perchlorate, (0.001 *M* solution in acetonitrile), was prepared and standardized as described earlier[9]. Triton-X-100 (0.002%, Merck) in acetonitrile, was used as the suppressor.

The polarographic measurements were made with an Elico (India) pulse polarograph (model CL-90) with polarocard recorder (model LR-180) equipped with DME as working electrode, SCE as reference electrode and a coiled platinum wire as an auxillary electrode. Cyclic voltammetric measurements were carried out with a ECDA-001 electrochemical system (Con-Serv Enterprises) using platinum disc electrode as working electrode and silver/silver chloride (0.01 *M* in methanol) as reference electrode and platinum wire as an auxillary electrode. Nitrogen gas was purified by passing the gas through an alkaline solution of pyrogallol.

Procedure

Copper(II) perchlorate (5.0 ml, 0.001 *M* in acetonitrile) and 5.0 ml of each [$Zn(dtc)_2$] (0.001 *M* in acetonitrile) were taken separately in 50 ml glass stoppered flasks, diluted to 20 ml with acetonitrile and then mixed with 20 ml of TEAP (0.01 *M* in acetonitrile). Triton-X-100 (2 ml, 0.002% in acetonitrile) was added as suppressor and the final volume of the solution made to 50 ml with TEAP. Nitrogen gas was passed through each solution for 5 min. Thereafter, the differential pulse polarogram was recorded at room temperature (23±1°C) with following instrumental parameters: Initial potential = + 400 mV; Height of Hg pool = 3.5 cm; h_{eff} value = 150 cm; CC compensation =5.0; IR compensation = 0; time constant = 20 ms; drop time = 1 s; pulse amplitude = 50 mV; acquisition = fast; O/P zero = 485; scan = normal; sensitivity = 1 μA/V; X-axis = 100 mV/cm and Y-axis = 200 mV/cm (on polarocord).

Aliquots (0.06-1.0 ml) of the stock solution (10^{-4} *M* in acetonitrile) of each [$Zn(dtc)_2$] in acetonitrile were taken in the polarographic cell containing 5.0 ml of copper(II) perchlorate (0.001 *M* in acetonitrile) and the volume was made to 20 ml with acetonitrile. Triton-X-100 (2 ml, 0.002% in acetonitrile) was added and the final volume was made up to 50 ml with TEAP (0.01 *M* in acetonitrile). Nitrogen gas was passed through each solution for 5 min and thereafter, differential pulse polarogram was recorded with the above instrumental parameters. The differential pulse polarograms resulting from the reaction of copper(II) perchlorate with [$Zn(dmdtc)_2$] and copper(II) perchlorate with [$Zn(dpdtc)_2$] is shown in Fig 1. The typical electrochemical characteristics resulting from the above studies are presented in Table 1. Calibration

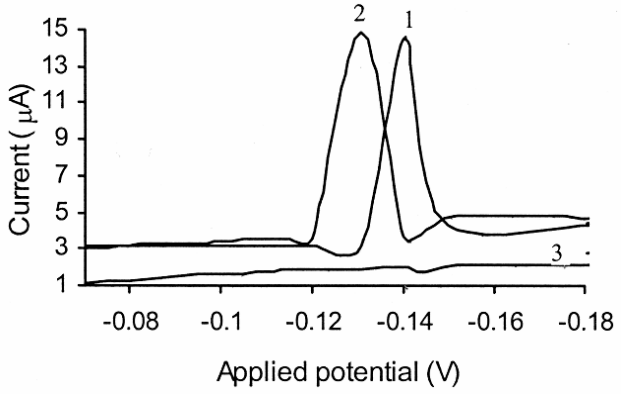


Fig. 1 — Typical differential pulse polarograms [1, copper(II)-zinc dimethyldithiocarbamate reaction; 2, copper(II)-zinc-di-*n*-pentyldithiocarbamate reaction; 3, supporting electrolyte at DME]

Table 1 — Electrochemical and calibration characteristics of zinc dithiocarbamates $Zn(dtc)_2$

Zinc dithiocarbamate	Peak potential (mV)		Linearity range (μg mL^{-1})	Slope	Intercept
	With $Zn(dtc)_2$ alone	With copper(II) perchlorate			
Dimethyl	240	-140	1.8-24.4	0.1147	-0.0026
Diethyl	230	-114	2.1-28.0	0.2114	0.0007
Di-*n*-propyl	224	-110	2.5-33.3	0.2217	-0.0040
Di-*n*-butyl	245	-105	2.8-35.5	0.1937	-0.0026
Di-*n*-pentyl	225	-130	3.2-37.0	0.1789	-0.0060

Table 2 —Recovery of ziram and vanlube AZ from commercial products[a]

Formulation	Active ingredient (%)	Amt taken (μg)	Amt found (μg)	Average recovery[b] (%)
Ziram (fungicide)	27	2.5	2.47 ±0.023	98.8 ± 0.9
		7.5	7.44 ± 0.075	99.2 ± 1.0
		15.0	14.76 ± 0.120	98.4 ± 0.8
		20.0	19.70 ± 0.140	98.5 ± 0.8
Vanlube AZ (petroleum additive)	100	3.0	2.95 ± 0.030	98.4 ± 1.0
		6.0	5.95 ± 0.048	99.1 ± 0.8
		12.0	11.91 ± 0.108	99.2 ± 0.9
		24.0	23.71 ± 0.190	98.8 ± 0.8

[a] Specification established by ref. method[1]
[b] Average results of three determinations.

graphs were constructed by plotting peak current (μA), (corresponding to the respective peak potentials given in Table 1) versus concentration of [$Zn(dtc)_2$] (μg) added to copper(II). The calibration characteristics are also given in Table 1.

One formulation each of ziram and vanlube AZ containing 27% and 100% active ingredient respectively were analysed. A single large sample of each formulation (23 mg of ziram and 7.5 mg vanlube AZ) was weighed, shaken with acetonitrile and filtered. The residue (if any) was washed 2-3 times with acetonitrile. The filtrate and washings were diluted to a known volume (25 ml) with the same solvent. Suitable aliquots of the solution were taken and processed for analysis as described above. The results are given in Table 2.

Results and discussion

The proposed pulse polarographic method has emerged during our studies on the mechanism of [$Zn(dtc)_2$]-copper(II) reaction in acetonitrile. This reaction had earlier afforded us potentiometric and photometric titration methods for the determination of [$Zn(dtc)_2$][9]. Though the stoichiometry of this reaction (1:2 molar ratio) has been established by the above methods, its mechanism had not been investigated till we used cyclic voltammetry (CV) to elucidate the same. The CV studies of $Zn(dtc)_2$-copper(II) reaction in acetonitrile medium using Pt-Ag/AgCl electrode assembly reveal that $Zn(dtc)_2$ alone do not show any current peak either in forward (negative) or reverse scan (positive) scan. Copper(II) perchlorate, on the other hand, shows a well-defined cathodic peak at 815 mV in forward scan and an anodic peak at 1040 mV in the reverse scan. Interestingly, when $Zn(dtc)_2$ was added to copper(II) perchlorate in acetonitrile and progress of the reaction was monitored quantitatively, it was observed that while the peaks belonging to the copper(II) reagent show a

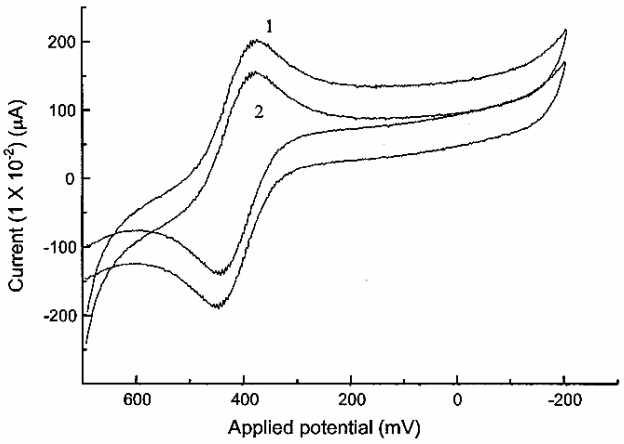
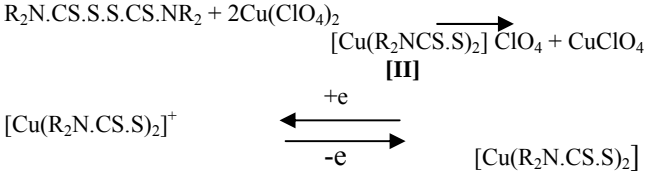


Fig. 2 — Typical cyclic voltammograms [1: copper(II)-zincdimethyldithiocarbamate reaction; 2, copper(II)-zinc di-pentyldithiocarbamate reaction at platinum electrode]

gradual decrease in current intensity, two new peaks, one in the forward scan (366-445 mV) and the other in the reverse scan (441-552 mV) showing ΔE value of 58-72 mV appear simultaneously with both showing proportional increase in current intensity. This behaviour continues till $Zn(dtc)_2$-copper(II) molar ratio of 1:2 is reached. At this point, the peaks belonging to copper(II) reagent disappears completely and each new peak attains full current intensity (Fig. 2). On the basis of above CV studies, the reaction between $Zn(dtc)_2$ and copper(II) can be represented to proceed with the formation of, most probably, copper(III) dialkyldithiocarbamate complex. It is this very complex which undergoes reduction in the forward scan and oxidation in the reverse scan and in doing so, it involves a one-electron change.

$$Zn(R_2N.CS.S)_2 + 2Cu(ClO_4)_2 \longrightarrow R_2N.CS.S.S.CS.NR_2 + 2Cu(ClO_4)_2 + Zn(ClO_4)_2$$

[I]



It has earlier been reported that copper(III) complexes of type **[II]** are in fact synthesized through the reaction of thiuram disulphides **[I]** and copper(I) perchlorate in acetonitrile, is quite well known [8,10-14]. The role of perchlorate ion (a bulky anion) in stabilizing the higher oxidation state of metals especially copper(III) dithiocarbamate complexes is quite well-known[11]. The stoichiometry of the complexation reaction resulting in the formation of **[II]** is supported by potentiometric and photometric titrations which are marked by well defined inflections/intersections at $Zn(dtc)_2$ to copper(II) molar ratio of 1:2. Also, the IR spectrum of **[II]** (acetonitrile solution) shows two bands at 1070 and 620 cm^{-1} indicating the presence of perchlorate group in the ionic form, i.e., outside coordination sphere. In the far IR spectrum of the product **[II]**, the appearance of additional band at 460 cm^{-1} reveals the formation of copper(III)-S bond[11]. The appearance of the two additional bands at λ_{max} 420 nm and 630 nm in the electronic spectrum of yellow product resulting from $[Zn(dtc)_2]$–copper(II) 1:2 reaction are characteristics of the above complexes of the type **[II]** [11,12,15].

The results of the present study as well as the earlier reported observations indicates that it is complex **[II]** which has generated the new analytically useful peak (at –105 to –140 mV, Table 1) which finds use in the present investigation as the basis of the proposed method. The method is quite sensitive and can be employed for the determination of as little as 1.8 μg ml^{-1} of $[Zn(dtc)_2]$. Zinc dithiocarbamates in the range 2.5-30.0 μg can be determined with maximum relative standard deviation (RSD) of 1.05%. The method when applied to the assay of ziram (a fungicide based on $[Zn(dmdtc)_2]$) and vanlube AZ (a petroleum additive based on $[Zn(dpdtc)_2]$) gave recoveries in the range 98.4-99.2% of the nominal content with RSD's in the range 0.8-1.0% (Table 2). The maker's specifications of each formulated products has been established separately by independent method[1].

Acknowledgement

The authors are indebted to Prof. B C Verma, Himachal Pradesh University, for his guidance and advice.

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