

A Polarographic and Voltammetric Study of Dithizone

Osman Çakır¹, Ender Biçer^{2*} and Emine Ertürk¹

¹Department of Chemistry, Faculty of Art and Sciences, Ondokuz Mayıs University, 55139 Samsun, TURKEY

²Department of Chemistry, Faculty of Education, Ondokuz Mayıs University, 55100 Samsun, TURKEY

ABSTRACT

The polarographic and voltammetric reduction of dithizone (1,5-diphenylthiocarbazone, H₂Dz, thiol form I) has been studied in Britton-Robinson buffers (pH 2.10-12.00) containing 50% ethanol at room temperature. The reduction of the compound takes place in single 2e⁻ transfer, giving a diffusion controlled reversible wave in the entire pH range of the study corresponding to the reduction of the azo group. A mechanism is proposed for the reduction process of the compound.

KEY WORDS: Dithizone, Polarography, Voltammetry.

INTRODUCTION

The polarographic investigation of aromatic azo-compounds has been the subject of several studies owing to their use in medicine and dyeing of textile fibres and as powerful chelating agents (1-3).

The polarographic behaviour of azo compounds in aqueous and non-aqueous media has been studied by various workers in the past. It is clear from these studies that even the simple azo compound, azobenzene, exhibits a complicated electrochemical behaviour (4, 5). However the introduction of substituent groups into the aromatic rings can completely change the nature of the electrode reaction (6, 7). The polarographic reduction of some azo compounds involves the consumption of four or two electrons in acid or in alkaline media, respectively (8, 9). Holleck indicated that the polarographic reduction of p-nitroazobenzene is wholly reversible in the pH range 1.9-12, in contrast to the substituted azobenzene and other substituted azo compounds (10).

Malik et al. during their studies on 1-thiocarbamoyl-3,5-dimethyl-4-phenylazopyrazole and

* To whom correspondence should be addressed.

1-thiocarbonyl-3,5-diphenyl-4-phenylazopyrazole containing thion group like H₂Dz, observed a 2e- reversible reduction wave corresponding to reduction of azo group (2).

Enethiol-thione tautomerisms were readily studied polarographically since the thiol form is reduced at potentials considerably more positive than the thione reduction. Thus, when the thiol exists in equilibrium with the thione, polarographic waves can be observed for both forms (11).

H₂Dz has been widely used in analytical chemistry since it forms highly colored inner sphere complexes with some metal ions such as copper, mercury and nickel (12,13). Dithizone is a diprotic acid. In its first protolysis, dithizone (pK₁ =4.82) is almost as strong as acetic acid (pK=4.56), but the second protolysis (pK₂ >15) is negligible. At pH values greater than 4.82, HDz⁻ becomes predominant (14). Literature survey reveals that in spite of the polarographic studies of several thion (C=S) and azo (N=N) compounds, the polarography of dithizone has not been systematically studied so far (15,16). In this compound represented in (I) the possible reduction sites are -SH or -C=N or -N=N-. Of these, the latter site should be more susceptible to reduction then the other two sites which would require a much higher negative potential for reduction.



(I)

EXPERIMENTAL

A polarographic analyzer EG&G Princeton Applied Research (PAR) Model 384B was used in all experiments. EG&G PAR Model 303A three-electrode system was used in the hanging mercury drop electrode (HMDE) mode for cyclic and square wave voltammetry, and in the dropping mercury electrode (DME) mode for sampled direct current polarography measurements. HMDE and DME were working electrodes. The three-electrode system was completed by means of a platinum wire counter electrode and a saturated Ag/AgCl reference electrode. In sampled direct current polarography, cyclic and square wave voltammetry, the potential scan increment was 2mV. Also in sampled direct current polarography, the drop time was 1.0 s. H₂Dz stock solutions, (4x10⁻³ M), were prepared by dissolving the pure substance (Merck, p.a.) in ethanol. Volumes of 100μL of these solutions were added in the cell, to 10mL of Britton-Robinson buffer which acted as the supporting electrolyte. Britton-Robinson buffers were made by mixing 40mL of 0.04 M boric acid, 40mL of 0.04 M

phosphoric acid and 40mL of 0.04 M acetic acid in water with 120mL of absolute ethanol. The pH of solution was adjusted to different values by addition of 1M NaOH (in a 1:1 water-ethanol solution). A Crison microPH 2000 / Digital pH-meter was used for pH measurements. Boric acid, phosphoric acid and acetic acid solutions were prepared in double distilled and deionized water. All the chemicals employed were of p.a. purity. Experiments were carried out at 20 °C in solutions degased by bubbling oxygen-free nitrogen for 300s . During the experiments the solutions were kept under a blanket of oxygen-free nitrogen.

RESULTS AND DISCUSSION

As can be seen in Fig. 1 , H₂Dz exhibits a single polarographic wave, assigned to the reduction of the azo group, in the sampled direct current polarograms (DCP), square-wave voltammograms (SWV) and cyclic voltammograms in the pH range of 2.10-12.00.

The polarographic and voltammetric characteristics of H₂Dz in Britton-Robinson buffers containing 50% ethanol at different pHs are summarized in Table 1. The reversibility of the electrode process was examined using sampled direct current polarography and cyclic voltammetry. In order to elucidate the mechanism for the reduction of H₂Dz, the number of electrons (n) involved in the electroreduction process was calculated using the relation :

$$E = E_{1/2} - \frac{0.059}{n} \log \frac{I}{I_d - I}$$

(where E = potential, E_{1/2} = half-wave potential, I = current , and I_d = diffusion current).

The values of the slopes of plots of E vs. log I / (I_d - I) lie in the range of 1.80 to 1.88, suggesting a reversible nature of the electrode reaction and also showing the involvement of two electrons in the reduction of azo group. It was observed that the n value was independent of pH. The reduction process is diffusion controlled, as deduced from the linear relationship between peak current and concentration of H₂Dz. The anodic (E_{pa}) and cathodic (E_{pc}) peak potentials were -0.610 and -0.642 V for the scan rate of 400 mVs⁻¹ at pH 9.20, respectively (Fig. 1c). The separation of peak potentials is close to the expected value (29 mV) for a two-electron transfer.

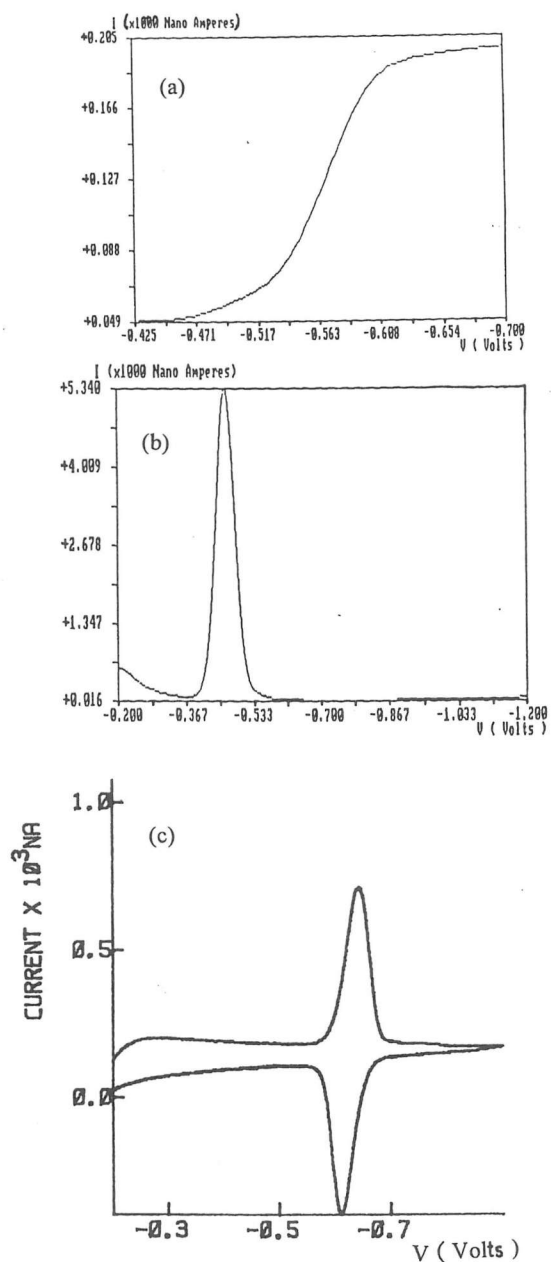


Fig. 1. Polarograms and voltammograms of H₂Dz in Britton-Robinson buffers containing 50% ethanol (a) DCP at pH= 8.40 ; (b) SWV at pH= 6.80 ; (c) CV at pH= 9.20

Table 1. The polarographic and voltammetric data obtained for H₂Dz in the pH range 2.10-12.00 (20 ° C)

pH	DCP E _{1/2} / V	SWV E _p / V	CV E _{pc} / V
2.10	-0.194	-0.194	-0.196
2.40	-0.214	-0.216	-0.218
2.80	-0.234	-0.236	-0.238
3.20	-0.258	-0.258	-0.260
3.60	-0.278	-0.280	-0.282
4.00	-0.300	-0.304	-0.304
4.40	-0.324	-0.326	-0.326
4.80	-0.348	-0.350	-0.348
5.20	-0.366	-0.370	-0.364
5.60	-0.388	-0.390	-0.392
6.00	-0.414	-0.416	-0.408
6.40	-0.436	-0.440	-0.438
6.80	-0.460	-0.464	-0.464
7.20	-0.484	-0.486	-0.490
7.60	-0.512	-0.514	-0.516
8.00	-0.540	-0.536	-0.542
8.40	-0.568	-0.562	-0.566
8.80	-0.594	-0.590	-0.596
9.20	-0.640	-0.638	-0.642
9.60	-0.644	-0.640	-0.646
10.00	-0.676	-0.670	-0.674
10.40	-0.700	-0.694	-0.700
10.80	-0.720	-0.716	-0.722
11.20	-0.742	-0.736	-0.744
11.60	-0.764	-0.758	-0.766
12.00	-0.782	-0.774	-0.782

E_p - pH Curves

The SWV, CV and DCP data obtained for the compound (20 °C) are presented in Table 1. As the pH is increased the peak potential E_p shifts to more negative values indicating that E_p is pH dependent and H⁺ ions take part in the electrode reaction (Fig. 2). The E_p-pH plots give a straight line on SWV, CV voltammograms and DCP polarograms.

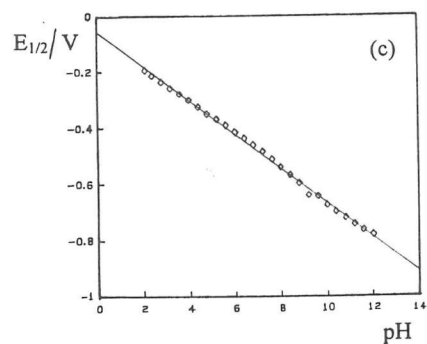
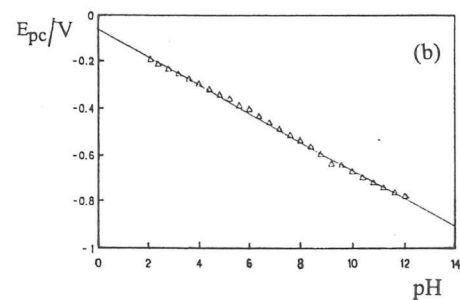
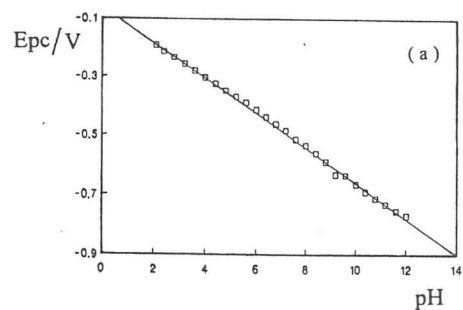


Fig. 2. Dependence of E_{pc} on pH: (a) SWV; (b) CV; (c) DCP

The observed of the peak potentials by increasing pH is in agreement with the following relationship in the pH range of 2.10-12.00 :

$$E_p = -0.0633 - 0.0597 \text{ pH} \quad (\text{SWV})$$

(correlation coefficient $r = 0.9982$) ; and

$$E_p = -0.0599 - 0.0607 \text{ pH} \quad (\text{CV})$$

(correlation coefficient $r = 0.9989$) ; and

$$E_{1/2} = -0.0568 - 0.0609 \text{ pH} \quad (\text{DCP})$$

(correlation coefficient $r = 0.9989$)

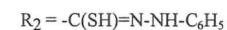
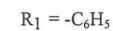
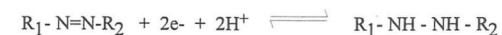
From the relation given below :

$$E_p / \text{pH} = 0.059 n / P$$

it can be concluded that the number of electrons consumed is equal to the number of protons (P) contributing to the electrode reaction of the azo group in the pH 2.10-12.00 (17-19).

The electrode reaction

By analogy with other azo compounds (20-22) it is possible to postulate - in agreement with above results - a reaction mechanism (for HDz^- in the $\text{pH} \geq 5.0$), in the pH range 2.10-12.00, as follows:



However, in alkaline medium, the proton needed for the reduction mechanism are obtained from the aqueous medium.

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PROGRESS IN ION CONTAINING ORGANIC POLYMERS

M.J.C. PLANCHA, C.M. RANGEL and C.A.C. SEQUEIRA

INETI - Materials Technology Department

Paço do Lumiar, 22, 1699 Lisboa Codex, Portugal

Abstract

Increased interest in highly conducting polymer electrolytes is clearly evident from the open literature, particularly on the specific area of energy-related applications. Poly(ethylene oxide), PEO, although well studied, continues to intrigue us and must still be regarded as playing a central role in polymer electrolyte research and development. Ion containing organic polymers involving essentially PEO as the solvent matrix are reviewed here. The greatest technological driving force for its continued study is still, by far, the desire for thin film rechargeable batteries that meet a multitude of ambitious energy, power density and safety requirements, while not being prohibitively expensive.

1. Introduction

During the last decade, appearance of ionically and electronically conductive polymers led immediately to their use as active components in new battery designs, as electrodes or electrolytes. They include the advantage of polymer materials as plasticity, good mechanical properties, easy processing and light weight in the area of solid state electrochemistry.

Our purpose here deals only with ion containing organic polymers: the organic polymer electrolytes. They alloy plasticity and mechanical properties of polymers to conductivity performances near that of liquids