

Electrochemical Behaviour of Hexa[4-(phenylazo)phenoxy]cyclotriphosphazene

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Received 16.06.1998

The polarographic and voltammetric behaviour of hexa[4-(phenylazo)phenoxy]cyclotriphosphazene in tetrahydrofuran-water 50% (v/v) was studied at room temperature using various electrochemical techniques. In this study, the reduction of the azo group to the amino group of the organophosphazenes compound was observed as the electrode reaction. An electrode reaction mechanism was suggested for the compound.

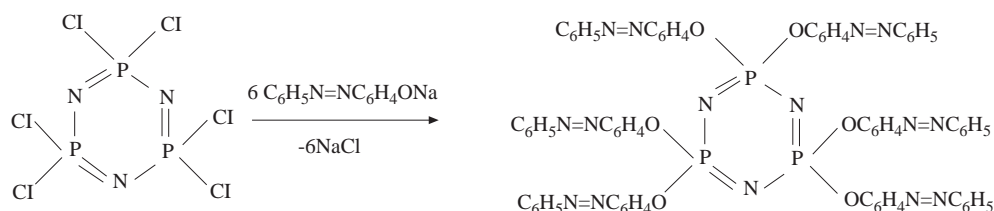
Key words: Voltammetry, phosphazenes derivatives.

Introduction

Azo dyes are widely used as additives in many products such as foods, drugs and cosmetics. Their potential carcinogenicity and the possibility of their inhibiting growth of animal tumours has led to studies of their polarographic reduction which parallels the metabolism of such compounds in vivo^{1,2}.

Aromatic azo dyes have been the subject of many polarographic and voltammetric investigations, which have shown that even the simplest of those compounds has complicated polarographic and voltammetric behaviour. The introduction of substituent groups into the aromatic ring can completely change the nature of the electrode reaction mechanism³⁻⁹.

Polarographic and voltammetric studies of azo compounds, especially those containing the hexa[4-(phenylazo) phenoxy]cyclotriphosphazene, are scarce. The aim of this study was to determine the polarographic and voltammetric behaviour of hexa[4-(phenylazo) phenoxy]cyclotriphosphazene. The compound was synthesized in our laboratories^{10,11} by modifying the method of Allock¹².



Scheme 1.

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Experimental

A polarographic analyser, EG&G Princeton Applied Research Model 384B with a PAR Model 303A static mercury drop electrode, was used. The sample cell (PAR model 6062) was fitted with a saturated Ag/AgCl reference electrode and a platinum wire auxiliary electrode. Polarograms and voltammograms were recorded by a DMP-40 Series Digital Plotter. The measurements were made at room temperature after deaerating with purified nitrogen for 300 s. The potential scan increment was 4 mV for Direct Current Polarography (DCP), Differential Pulse Polarography (DDP) and Square Wave Voltammetry (SWV) and for all samples and the DCP and DPP drop time was 1.0 s.

0.050 g/50ml stock solution of hexa[4-(phenylazo) phenoxy]cyclotriphasphazene was prepared in tetrahydrofuran. Other chemicals used were analytical grade. All solutions were prepared using triple distilled water.

Britton-Robinson buffer prepared in tetrahydrofuran-water 50% (v/v) solution with different pH values was used as the supporting electrolyte. 100 μ l of stock solution was added to 10 ml electrolyte at different pH values.

Results and Discussion

The effect of the pH on the current-voltage curves was investigated by recording polarograms and voltammograms of hexa[4-(phenylazo) phenoxy]cyclotriphasphazene solution of tetrahydrofuran-water 50% (v/v) in Britton-Robinson buffer. Hexakis-4-(phenylazo) phenoxy cyclotriphasphazene exhibits a single peak through the whole pH range studied (Fig. 1).

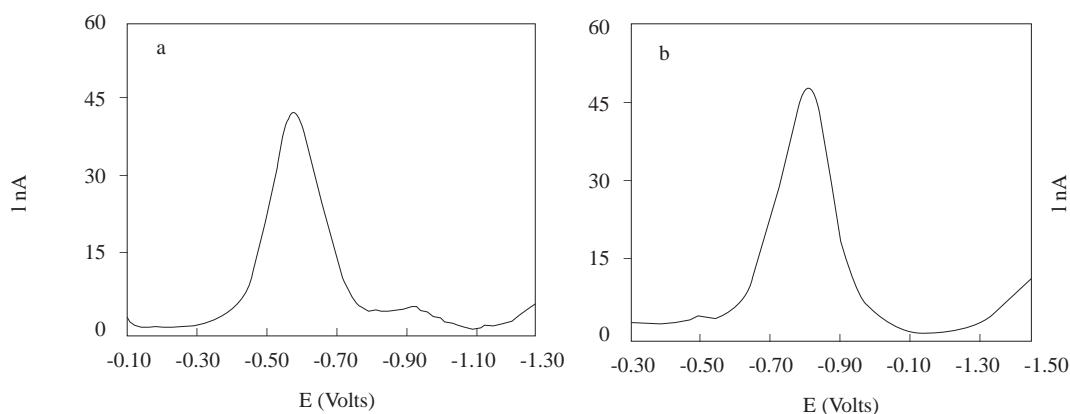


Figure 1. Polarogram and voltammogram of the compound in Britton Robinson buffer solution a) DPP at pH=5.70, b) SWV at pH=6.90

The plot of E_p vs. pH (Fig. 2) shows two lines portions with a break at pH 8.0, corresponding to the change of the electrode reaction mechanism for the phosphazenes. The variation of the slopes of the curves is dependent on the nature of the reactant. From the relation given below, it can be concluded that the number of electrons (n) consumed equals that of the protons (p) that contribute to the electrode reaction;

$$E_p/pH = 0.059 p/n$$

As shown in Figure 2, the peak potential of the compound shifts linearly to more negative potentials with increasing pH indicating that hydrogen ions contribute to the electrode process¹³. In the first linear

part (pH range 3.0-7.0) the peak potential may be expressed by the equation:

$$E_p = -0.0557 \pm 0.0021 - 0.0974 \pm 0.051 \text{pH} \quad (r^2 = 0.9756 \text{ for DPP})$$

$$E_p = -0.1428 \pm 0.0102 - 0.0970 \pm 0.0024 \text{pH} \quad (r^2 = 0.9800 \text{ for SWV})$$

The peak current is also pH dependent. While increasing pH, the peak current decreases until pH < 6 and stays approximately constant at higher pH values (Fig. 3).

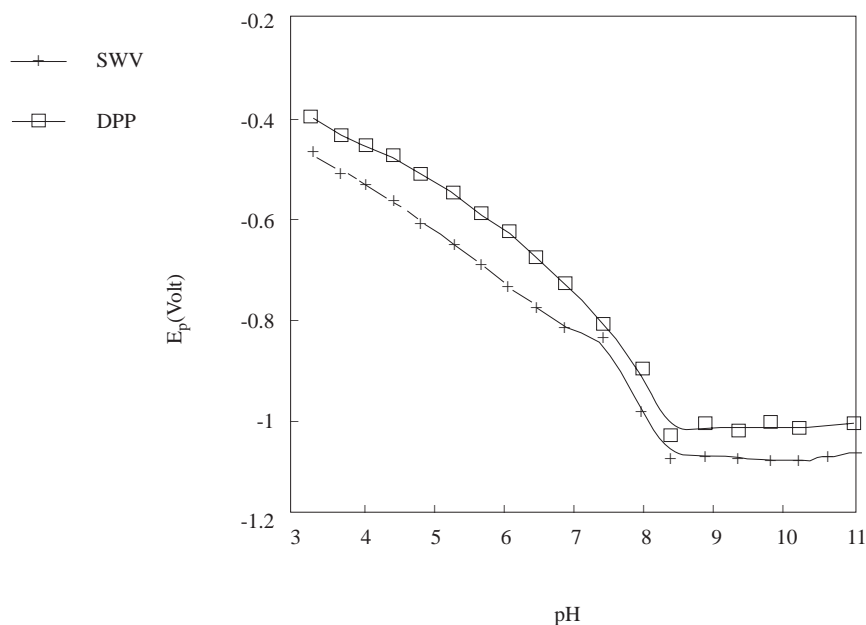


Figure 2. pH dependence of the E_p for the compound a) DPP and b) SWV

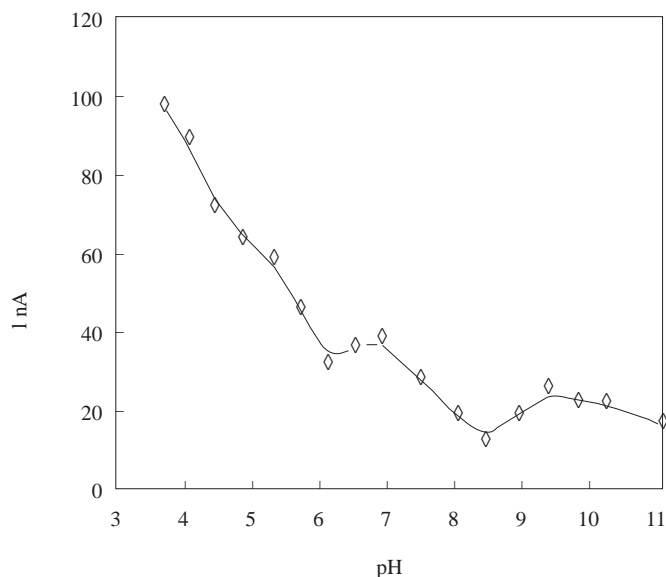


Figure 3. pH dependence of the I_p for the compound at DPP

The reversibility of the electrode process was studied using simple dc and cyclic voltammetry. From logarithmic analysis of $\log(I/I_d - I)$ vs. E of the simple dc polarograms, αn values were obtained^{13,14}. As

can be seen in Fig. 4 the αn values are pH dependent. At $\text{pH} < 7$, αn values are dependent on the pH but not for higher pH values. It is observed in cyclic voltammetry that both anodic and cathodic peaks in the whole pH range indicate the irreversibility of the electrode process (Fig. 5). Particularly, at $\text{pH} > 7$ the adsorption effect was observed. This effect can be demonstrated by the asymmetric shape of the peak in the cyclic voltammograms¹⁴.

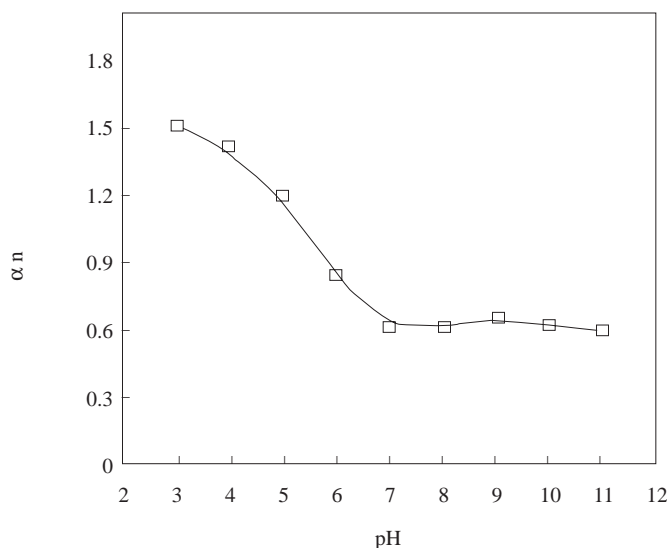
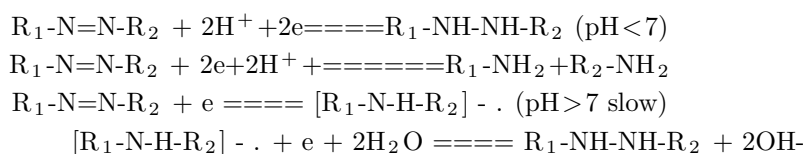


Figure 4. pH dependence of αn for the compound.

In the literature the reduction of organophosphazenes compounds was studied in organic solvents because of insolubility in water^{15,16}. In subsequent studies, the organophosphazene compounds were electroinactive. However, some organophosphazenes compounds with several substituents have shown a reduction peak^{12,15}. In this study, a single peak was observed for the compound which was compared with 4-hydroxyazobenzene. This peak belongs to the azo group in the compound. Similar results were also obtained for the azo group in dyes^{2-9,17,18}. As shown in Fig. 2 the electrode reaction mechanism is in the type of the proton addition but the slope of E_p versus pH plot is different from 0.059p/n in both SWV and DPP. At the same time, the value αn shows that the electrode reaction is quasi-irreversible due to the difference from theoretically calculated values (Fig 4).

The electrode reactions which belonged to azo groups were changed to hydrazo or aniline derivatives dependent on the solvent and substituent effect. In acidic media, the ratio of the anodic peak to the cathodic peak (I_{pa}/I_{pc}) was lower than 1.0 (Fig. 5). Nevertheless, the difference between the anodic peak potential and cathodic peak potential was much higher than $0.059/\text{n}$. The results in acidic media support the electrode reaction of the azo group changing to aniline derivatives. Asymmetric peaks were observed with increasing pH in the polarograms and voltammograms. In basic media, it was concluded that the electrode reaction followed a two step mechanism (Fig 2-5). This speciality was observed on changing αn -pH.

Therefore, overall the evidence is consistent with the electrode reaction mechanism belonging to hexa[4-(phenylazo) phenoxy]cyclotriphosphazene:



In conclusion all the criteria applied indicated that the reduction showed a quasi-irreversible process.

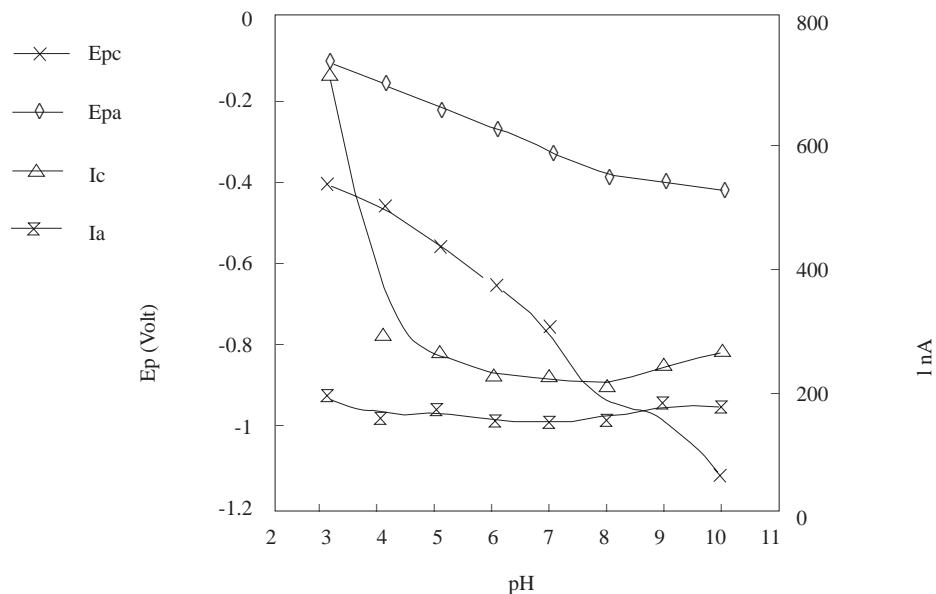


Figure 5. pH dependence of cathodic peak, anodic peak potential and current for the compound.

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