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Polarographic Behaviour of 1,3-Bis[(2-pyridyl)methyleneamino]thiourea (*PMAT*) in Absence and Presence of Triton X-100

Ali Z. Abu Zuhri

Chemistry Department, Faculty of Science, An-Najah National University,
Nablus, West Bank, Via Israel

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The polarographic behaviour of 1,3-bis[(2-pyridyl)methyleneamino]thiourea (*PMAT*) in solutions of varying *pH* has been studied both in the absence and presence of Triton X-100 (T.X-100). The mechanism for the reduction process is discussed. The adsorption effect of electrochemically inactive T.X-100 on the polarographic waves of *PMAT* has been investigated. The values of the kinetic parameters for the electrode reaction at different *pH* values have been computed. The applicability of the polarographic method for determination of *PMAT* is also discussed.

[Keywords: Polarographic behaviour; Triton X-100; 1,3-Bis[(2-pyridyl)-methyleneamino]thiourea (PMAT)]

Das polarographische Verhalten von 1,3-Bis[(2-pyridyl)methylenamino]-thioharnstoff (PMAT) in Anwesenheit und Abwesenheit von Triton X-100. Die polarographische Bestimmung von PMAT

Es wurde das polarographische Verhalten von *PMAT* in Lösungen mit verschiedenem *pH* sowohl in Gegenwart als auch ohne Triton X-100 (T.X-100) untersucht. Es wird ein Mechanismus für den Reduktionsprozeß diskutiert. Der Adsorptionseffekt des elektrochemisch inaktiven T.X-100 wurde hinsichtlich der polarographischen Wellen von *PMAT* untersucht. Die kinetischen Parameter der Elektrodenreaktion wurden für verschiedene *pH*-Werte ermittelt. Ebenso wird die Anwendbarkeit der polarographischen Methode für die Bestimmung von *PMAT* diskutiert.

Introduction

Recently, the possibilities for analytical use of pyridine thiosemicarbazide and thiocarbohydrazide have been reported [1, 2]. These compounds are interesting substances with numerous biochemical, pharmacological, industrial and other uses. Attention is now focused on the use of the 1,3-bis[(2-pyridyl)methyleneamino]thiourea (*PMAT*) for a photometric determination of metal ions [1]. The polarographic behaviour of different compounds containing —HC = N—NH—CO— or —CH = N—NH—CS— groups has been studied [3–7]. However, a literature survey revealed the lack of polarographic data on *PMAT*.

The present work represents an investigation of the polarographic behaviour of *PMAT* in buffer solutions of varying *pH* containing 50% ethanol in order to throw some light on the reduction mechanism. The kinetic parameters of the electrode reaction are also determined. The effect of Triton X-100 (*SAS*) on the polarographic waves was also studied.

Experimental

1,3-bis[(2-pyridyl)methyleneamino]thiourea (*PMAT*) was prepared according to a standard procedure [1]. A $4.0 \cdot 10^{-3}$ *M PMAT* solution was prepared by dissolution of an appropriate amount of solid in hot ethanol. As supporting electrolytes the universal buffer series of *Britton* and *Robinson* [8] was used.

The average current—voltage curves were recorded by a polarograph, model 3001 (Sargent Welch). The electrode characteristics were $m = 1.53\,\mathrm{mg\,s^{-1}}$ and $t = 4.9\,\mathrm{s}$ at a mercury height of 57 cm. The coulometric method of *De Vries* and *Kroon* [9] using a mercury pool cathode was used for determining the value of *n*, the number of electrons involved in the reaction process.

Results and Discussion

Behaviour in the Absence of Triton X-100

The polarograms of $4.0 \cdot 10^{-4}$ *M PMAT* at the dropping mercury electrode (d.m.e.) each consist of a single irreversible wave (Fig. 1). Whithin the *pH* range 1.89–10.7 the half wave potential ($E_{1/2}$) of this wave shifted to more negative values with increasing *pH* of the solution, indicating that the H^+ ions are involved in the electrode reaction. Above *pH* 10.7, the $E_{1/2}$ is practically *pH*-independent. In buffer solutions of *pH*'s 1.89–3.44 an apparent maximum is observed which can be eliminated by the addition of Triton X-100 (T.X-100). The height of the wave was practically constant within the whole *pH* range.

The $\Delta E_{1/2}/\Delta pH$ relation of the wave is a straight line with a slope equal to 0.053 in the *pH* range 1.89–10.7 (Fig. 2). This slope indicates that one H^+ ion per electron is consumed in the rate-determining step, because $\Delta E_{1/2}/\Delta pH = X_{H^+}\,(0.059/\alpha n_a)$; X_{H^+} and n_a represent the number of H^+ ions and electrons involved in the rate-determining step, respectively.

In order to test the validity of the *Ilkovic* equation and the applicability of the polarographic method for the determination of *PMAT*, the total

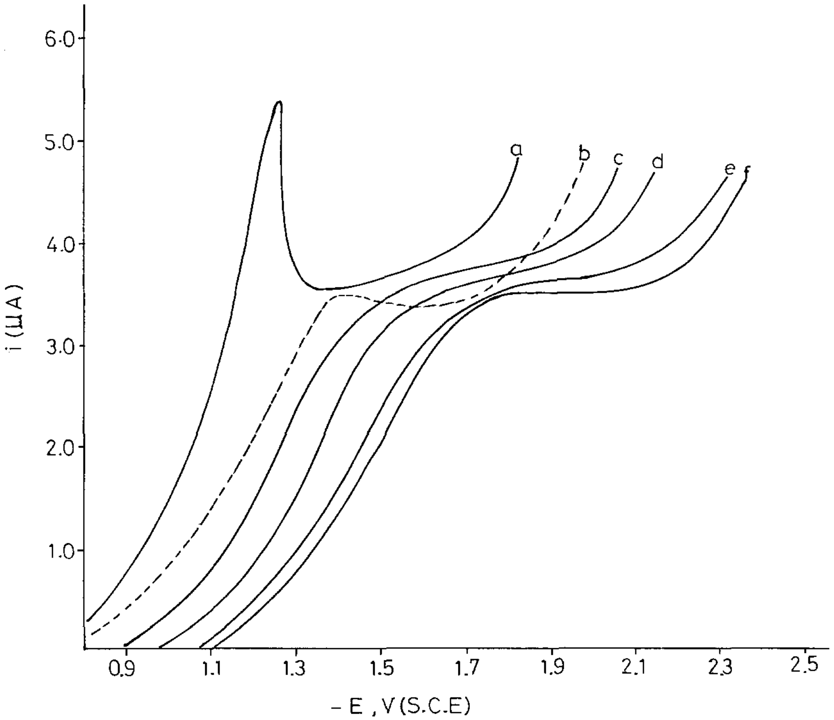

Fig. 1. Effect of *pH* on $4 \cdot 10^{-4} M$ *PMAT* in 50% ethanol: *a pH* 1.89; *b* 3.41; *c* 5.44; *d* 7.34; *e* 9.64; *f* 10.70

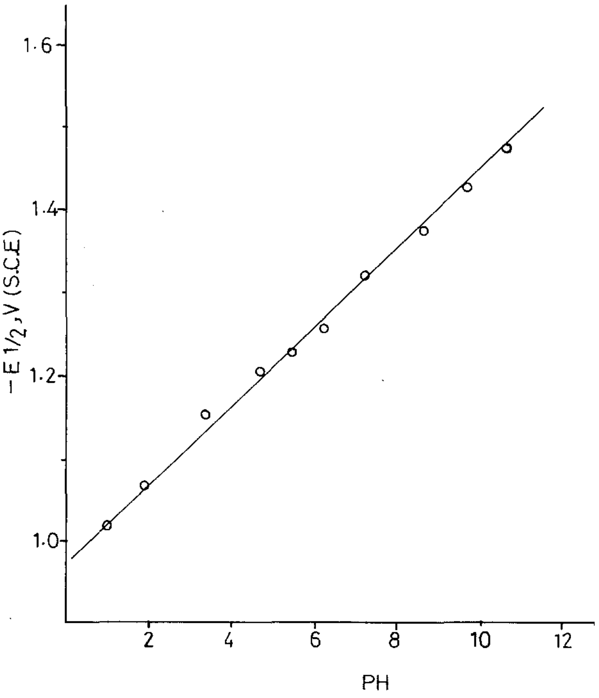

Fig. 2. $E_{1/2}$—*pH* plot

limiting current at different *pH*'s (acidic-neutral—alkaline) is plotted as a function of the concentration of the depolarizer ($1.0 \cdot 10^{-4}\,M$—$1.0 \cdot 10^{-3}\,M$). Satisfactory linear relations passing through the origin are obtained.

Reduction Mechanism

In order to find out the mode of reduction of *PMAT* at d.m.e., it was necessary to calculate the number of electrons consumed in the electroreduction process by applying the *Ilkovic* equation. The value to the diffusion coefficient (D) is not available and can be calculated from the relation:

$$D = \frac{3.22 \cdot 10^{-5}}{(V_m)^{1/3}}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$$

V_m is the apparent molar volume of the substance in the solid state, and is equal to molecular weight/density (284.64/1.11). The value of D thus obtained corresponds to that in aqueous solutions. For use in 50% ethanol solutions, the effect of viscosity of the medium must be accounted for. The corrected value of D_{alc} can be obtained from the relation:

$$\frac{\eta_{\mathrm{alc}}}{\eta_{\mathrm{aq}}} = \frac{D_{\mathrm{aq}}}{D_{\mathrm{alc}}}$$

Thus, by applying the *Ilkovic* equation, the number of electrons involved in the electrode reaction at different *pH* values can be calculated as given in Table 1. From the data given in Table 1 it is evident that two electrons were consumed in the process of reduction in the *pH* range 1.89–10.7. The coulometric experiments applied at potentials on the plateau of the polarographic curve verified a consumption of two electrons per molecule in the above *pH* range.

It is obvious that the compound contains two reducible centres $C=N$ and $C=S$. The $C=S$ is inactive towards reduction as a result of the mesomeric effect with the neighbouring imine group. This fact was confirmed by *Temerk* [6, 9] and *Issa* [4, 5] for a similar compounds. The alternative reductive splitting of the N—N · bond is highly improbable due to the fact that the compound thiocarbohydrazide (H_2N—NH—CS—NH—NH_2) was found to be polarographically inactive in the available potential range as was proved experimentally. This is in accordance with the fact that the reduction step of N—N would involve the break down of the more stable N—N bond. Accordingly the azomethine linkage should be the active centre to be reduced. Thus the electrode reaction for *PMAT* can be considered to take place as follows:

$$\mathrm{NH_4C_5{-}HC{=}N{-}NH{-}CS{-}NH{-}N{=}CH{-}C_5H_4N} + 2\,\mathrm{e} + 2\,\mathrm{H}^+ \rightarrow$$
$$\mathrm{NH_4C_5{-}H_2C{-}NH{-}NH{-}CS{-}NH{-}N{=}CH{-}C_5H_4N}$$

Table 1. *Kinetic parameters of* $4 \cdot 10^{-4}$ *M PMAT in different buffer solutions containing 50% ethanol*

pH	$-E_{1/2}$, V	$\Delta E_{1/2}/\Delta pH$		$\frac{0.059}{\alpha n_a}$	αn_a	Polarographic (n) values	slope of $\log i - \log h$ plot	K_0 cm/s	$K_0 D^{-1/2}$ ($K = K_0$)	ΔG^* kcal/mol
		pH range	slope							
1.89	1.06	1.89–10.7	0.053	0.35	0.17	1.95	0.58	$1.82 \cdot 10^{-10}$	$1.15 \cdot 10^{-7}$	85.74
5.44	1.23			0.30	0.20	1.95	0.55	$4.37 \cdot 10^{-11}$	$2.76 \cdot 10^{-8}$	89.32
7.34	1.32			0.30	0.20	1.92	0.56	$1.85 \cdot 10^{-11}$	$1.15 \cdot 10^{-8}$	91.51
10.7	1.47			0.20	0.30	1.87	0.56	$9.31 \cdot 10^{-13}$	$5.76 \cdot 10^{-10}$	99.03

Effect of Triton X-100

In presence of T.X-100, $E_{1/2}$ shifted to more negative potential on increasing the concentration of T.X-100 and approaches a constant value at relatively high concentration of T.X-100. Generally, the limiting current decreases with increasing concentration of the T.X-100. However, we can plot (Δi_l), the decrease of the limiting current with respect to the i_l value in the absence of T.X-100 for a given T.X-100 concentration as a function of the concentration of the T.X-100. The resulting curves have the form of an adsorption isotherm.

To follow quantitatively the adsorption effect of T.X-100 on the different wave parameters, the Δi_l at a given concentration of T.X-100 was determined and the degree of coverage Θ was evaluated with the relation

$$\Theta = \Delta i_l/(\Delta i_l)_m$$

where Δi_l is the decrease of limiting current with respect to the i_l value of the wave in absence of T.X-100 and $(\Delta i_l)_m$ the maximal decrease corresponding to full coverage. It has been found that the degree of coverage dependence of the concentration of T.X-100 (Fig. 3) fit well a *FrumKin* adsorption given by equation:

$$\frac{\Theta}{1-\Theta}\exp(-2a\Theta) = bC$$

Where Θ is the degree of coverage, a the interaction coefficient, b the adsorption coefficient and C the concentration of T.X-100.

The interaction coefficient (a) was determined from the slope of the logarithmic plot of the *FrumKin* isotherm and the adsorption coefficient (b) from the values at half coverage in the usual manner [10]. The free energy of adsorption ($-\Delta G^\circ$) was then calculated from the adsorption coefficient (b) according to equation

$$b = \frac{1}{55.5}\exp\left(\frac{-\Delta G^\circ}{RT}\right)$$

The calculated values of the adsorption parameters at *pH*'s 1.89, 5.44 and 10.7 are given in Table 2. The various parameters indicate that the surface activity of the T.X-100 increase by increasing *pH.*

Nature of the Wave in Absence and Presence of T.X-100

The effect of mercury pressure on the limiting current of the electroreduction of the wave in absence of T.X-100 indicated that the reduction waves are mainly diffusion controlled with slight adsorption

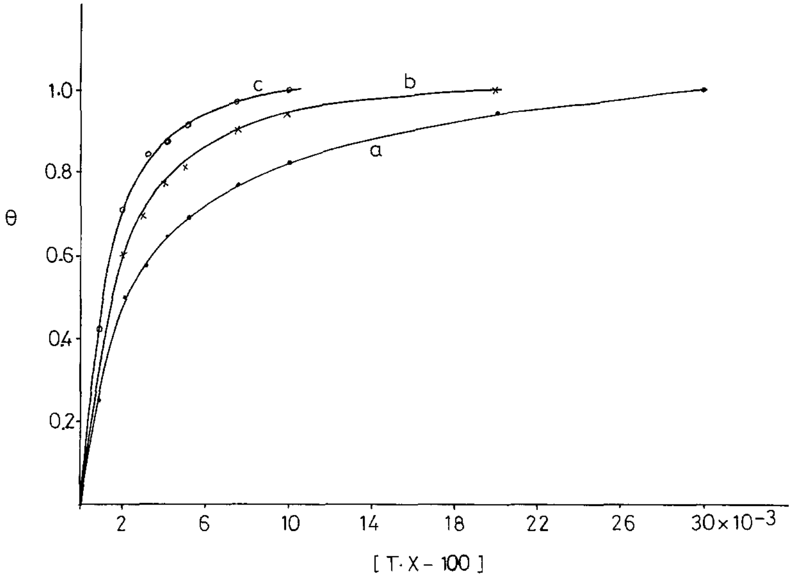

Fig. 3. Dependence of surface coverage θ on the bulk concentration of T.X-100 at different *pHs*: *a pH* 1.89; *b pH* 5.44; *c pH* 10.70

Table 2. *Adsorption parameters of T.X-100, calculated from the polarographic results at pH's 1.89, 5.44 and 10.7*

pH	*a*	*b* (l/mol)	—Δ *G*° (kcal/mol)
1.89	1.43	$5.0 \cdot 10^3$	7.47
5.44	1.01	$6.2 \cdot 10^3$	7.67
10.7	0.91	$9.9 \cdot 10^3$	7.86

contribution which increases in presence of T.X-100. This is obvious from the values of the exponent x in the relation ($i_l = Kh^x$), as given in Tables 1 and 2.

The analysis of the waves was carried out by applying the fundamental equation for the polarographic wave:

$$\Delta E/\Delta \log(i_d - i) = 0.059/\alpha n_a \quad \text{at} \quad 25\,^\circ\text{C}$$

The values of the slopes ($0.059/\alpha n_a$) in presence of T.X-100 (Tables 1 and 2) are higher than in its absence and tend to increase with increasing concentration of T.X-100, indicating that the reduction process in presence of T.X-100 becomes more irreversible.

Table 3. *Effect of Triton X-100 on the kinetic parameters of* $4 \cdot 10^{-4}$ *M PMAT at different pH values in presence of 50% ethanol*

pH	T.X-100 conc. %	$\frac{0.059}{\alpha n_a}$	αn_a	slope of $\log i - \log h$ *plot*	K_0 cm/s	$K_0 D^{-1/2}$ $(K = K_0)$	ΔG^* kcal/mol
1.89	$5.0 \cdot 10^{-3}$	0.42	0.14	0.62	$2.31 \cdot 10^{-14}$	$1.45 \cdot 10^{-11}$	108.27
	$4.0 \cdot 10^{-2}$	0.44	0.13	0.65	$6.82 \cdot 10^{-15}$	$4.27 \cdot 10^{-12}$	111.34
5.44	$7.5 \cdot 10^{-3}$	0.37	0.16	0.59	$4.50 \cdot 10^{-13}$	$2.82 \cdot 10^{-10}$	100.82
	$5.5 \cdot 10^{-2}$	0.40	0.15	0.61	$3.82 \cdot 10^{-13}$	$2.40 \cdot 10^{-10}$	101.22
7.34	$7.5 \cdot 10^{-3}$	0.34	0.17	0.61	$2.35 \cdot 10^{-12}$	$1.48 \cdot 10^{-9}$	96.66
	$5.0 \cdot 10^{-2}$	0.38	0.15	0.63	$3.14 \cdot 10^{-13}$	$1.95 \cdot 10^{-10}$	101.74
10.7	$9.0 \cdot 10^{-3}$	0.26	0.23	0.58	$4.55 \cdot 10^{-14}$	$2.89 \cdot 10^{-11}$	106.60
	$7.5 \cdot 10^{-2}$	0.30	0.20	0.64	$5.00 \cdot 10^{-14}$	$3.17 \cdot 10^{-11}$	106.37

Kinetic Parameters of the Electrode Reaction in Absence and Presence of Triton X-100

The different kinetic parameters for the electrode reaction including αn_a (α is the transfer coefficient, n_a the number of electrons involved in the rate determining step), K_0 (the rate constant at $E = 0$), $K_0 D^{-1/2}$ (D is the diffusion coefficient) and ΔG^* (free energy of activation) in absence and presence of T.X-100 were computed by the aid of the *Koutecky* [11] relations.

In the absence of Triton X-100, the various parameters indicate that the process of reduction is irreversible. This is shown by the fact that the value of α is less than unity. The values of activation energy ΔG^* increase and the values of rate constant (K_0) at $E = 0$ decrease with increasing *pH* confirming the increased irreversibility of the electrode reaction (Table 1).

The values of the kinetic parameters in the presence of Triton X-100 indicate that the degree of irreversibility increases slightly as the concentration of the Triton X-100 is increased (Table 3).

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