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Electrochemical Behavior of Thiopyrimidines in Aqueous-Acetone Media at Mercury Electrode

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ABSTRACT

Polarographic studies of 1-(phenyl) 4, 4, 6-trimethyl pyrimidine-2-thione (PPT) and 1-(4'-chlorophenyl) 4, 4, 6-trimethyl pyrimidine-2-thione (4CPPT) at Dropping Mercury Electrode (DME) reveal that the product of the anodic reaction is strongly adsorbed at the mercury surface, as indicated by a prewave. The anodic wave of the pyrimidines extends over a fairly wide span of potential. The current of the main wave is proportional to the concentration up to 0.60 mM of PPT and 0.90 mM of CPPT in acetone water mixture at DME. This electrode is used as indicator electrode for polarographic titration of pyrimidine-2-thiones.

Keywords: Polarography, pyrimidine-2-thione, DME.

INTRODUCTION

In recent years a lot of work has been reported on the polarography of thiocompounds[1-7].The presence of the functional group is responsible for their behavior. The thio compounds are mostly electro-oxidizable at the indicator electrode surfaces. Their polarographic responses were similar to those of common thiol compounds like potassium isobutyl xanthate [8], potassium octyl xanthate [9], sodium isopropyl xanthate[10], sodium pentamethylene-dithiocarbamate[11] and sodium ethyl xanthate[12]. The polarographic behavior of pyrimidine thiones have been studied with a view to explore the possibility of utilizing them as analytical reagents and their behavior in electrolytic cell. A number of polarograms of these pyrimidines were recorded using the dropping mercury electrode in various supporting electrolytes viz. $HClO_4$, KNO_3, H_2SO_4, Na_2SO_4 and NH_4Cl. Different buffer solutions used to maintain pH include borax, disodium hydrogen phosphate, potassium dihydrogen phosphate and potassium hydrogen phthalate.

MATERIALS AND METHODS

Instruments: A manual Toshniwal Polarograph (Toshniwal India, model CLO2A) in conjunction with the dropping mercury electrode, saturated calomel electrode with agar-agar KCl bridge was used for recording the polarogram. E.C.I.L.digital pH-meter was used for adjusting the pH.

Electrodes: Working electrode was the dropping mercury electrode. The mercury used was of analytical grade which was further purified by passing through aqueous nitric acid (10%) followed by washing with distilled water, drying and vacuum distillation. Calomel electrode was used as a reference electrode throughout the work and all potentials reported in this study were measured with respect to this electrode.

Electrochemical Cell: 50 ml Pyrex beaker was used as an electrochemical cell. It was fitted with a cap having holes for introducing the electrodes and nitrogen. Solution was deoxygenated by bubbling nitrogen gas and then maintained as anaerobic by passing nitrogen over the solution. The pH of the medium was varied using buffers of different pH. The solutions of pyrimidines were prepared by dissolving their requisite weights into 50% acetone (AnalaR) water (double distilled) mixture.

General Procedure: An aliquot of the compound 1-(phenyl) 4, 4, 6-trimethyl pyrimidine-2-thione (PPT) and 1-(4'-chlorophenyl) 4, 4, 6-trimethyl pyrimidine-2-thione (4CPPT) was taken in a beaker. The medium was adjusted to desired pH value. To this added sufficient gelatin, as maximum suppressor to render the final solutions 0.01% with respect to the compound solution. Then diluted it to 25ml with 50 % water-acetone and transmitted to a 50ml Pyrex beaker used as polarographic cell. It was deaerated by passing nitrogen through it and polarograms were recorded at 25 ±1°C.

RESULTS AND DISCUSSION

Effect of various supporting electrolytes and solvents: The effect of various supporting electrolytes has been studied for both the Pyrimidines by varying the concentration of the electrolytes from 0.02M-0.2M. A well defined anodic wave with a small pre-wave was obtained in all the cases. The nature of the wave remained unchanged and diffusion current and half-wave potentials were found to remain constant in the above range studied. Polarograms in different electrolytes such as KNO_3, $HClO_4$, H_2SO_4, KCl, $NaClO_4$, $(C_2H_5)_4NBr$, Na_2SO_4 and NH_4Cl had the same appearance. The diffusion current constant was found to increase in the following order :-$(C_2H_5)_4NBr>KNO_3>KCl>NaClO_4$.. This may be due to the variation in the viscosity of the solution (Iα1/viscosity) [13].

Effect of height of mercury column: Polarograms of 0.10mM of PPT and 0.15mM of 4CPPT solutions at various heights of mercury column showed the diffusion controlled nature of the wave. The values for $id/h^{1/2}$ Hg were found to be fairly constant (Table 1 and Table 2).

Table 1. Effect of the height of the mercury column on diffusion current of 1-(phenyl) 4, 4, 6-trimethylpyrimidine-2-thione (PPT)

Sr.No	Height of mercury column (cm.)	Diffusion current* (μA)	$id/h^{1/2}$ Hg
1	30	0.340	0.062
2	35	0.367	0.062
3	40	0.399	0.063
4	45	0.428	0.064
5	50	0.438	0.062
6	55	0.460	0.062

*corrected for the residual current. PPT concentration = 0.10 mM, Sensitivity = 10x
H_2SO_4 concentration = 0.1 M pH = 2

Table 2. Effect of the height of the mercury column on diffusion current of 1-(4'-chlorophenyl) 4, 4, 6-trimethylpyrimidine-2-thione (4CPPT)

Sr.No	**Height of mercury column (cm.)**	**Diffusion current* (μA)**	**id/h$^{1/2}$ Hg**
1	30	0.522	0.095
2	35	0.564	0.095
3	40	0.600	0.094
4	45	0.637	0.095
5	50	0.671	0.094
6	55	0.704	0.094

*corrected for the residual current. 4CPPT concentration = 0.15 mM
Sensitivity = 10x, H_2SO_4 concentration = 0.1 M, pH = 2

Effect of Pyrimidine concentration: Several polarograms with varying concentration of the pyrimidines were recorded (Fig. 1a and Fig. 2a) at pH 2.0. The plot of diffusion current versus concentration gave straight lines upto 0.60mM of PPT (Fig. 1b and Table 3) and 0.90 mM of 4CPPT (Fig. 2b and Table 4) The values of slope obtained from the log plots indicated irreversible nature of the waves and the value of $E_{1/2}$ obtained are -0.065V for PPT and -0.060V for 4CPPT.

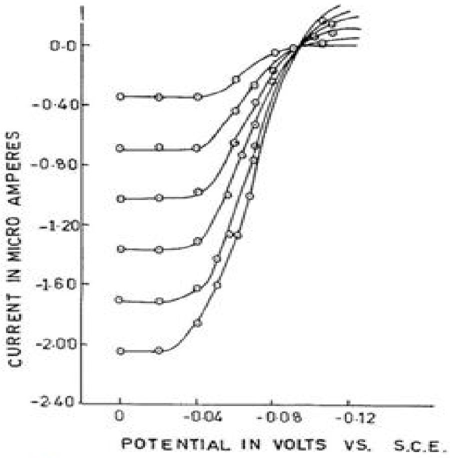

FIG.1a POLAROGRAMS OF 1-(PHENYL) 4,4,6-TRIMETHYL PYRIMIDINE- 2-THIONE

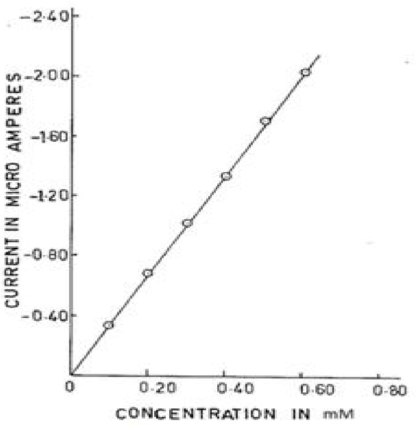

FIG. 1b PLOT OF DIFFUSION CURRENT VS. CONCENTRATION OF 1-(PHENYL) 4,4,6- TRIMETHYL PYRIMIDINE -2- THIONE

Table 3. Relation between diffusion current and 1-(Phenyl) 4, 4, 6 trimethylpyrimidine-2-thione (PPT) concentration.

Curve	**Concentration of PT (mM)**	**Diffusion current* (μA)**	**I= id/ C.m$^{2/3}$t$^{1/6}$**
A	0.10	0.340	1.504

B	0.20	0.678	1.500
C	0.30	1.038	1.528
D	0.40	1.350	1.493
E	0.50	1.680	1.486
F	0.60	2.062	1.520

*corrected for the residual current. H_2SO_4 concentration=0.1M, Senstivity=10x,
Flow rate of mercury=2.52 mg/sec. Temperature=25 ±1°**C,** Drop time=3.3sec. pH= 2

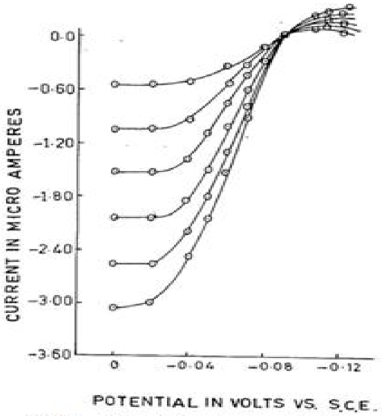

FIG. 2a POLAROGRAMS OF 1-(4'-CHLOROPHENYL) 4,4,6-TRIMETHYL PYRIMIDINE-2-THIONE

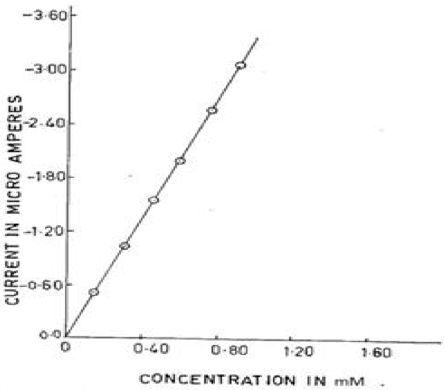

FIG. 2b PLOT OF DIFFUSION CURRENT VS. CONCENTRATION OF 1-(4'-CHLOROPHENYL) 4,4,6-TRIMETHYL PYRIMIDINE-2-THIONE

The mean value of diffusion current constant 'I' determined from the equation ($I = id/cm^{2/3}\ t^{1/6}$) was found to be 1.50 for PPT (Table 3) and 1.53 for 4CPPT (Table 4). Applying Lingane's equation [14] I=1.5n, the value of 'n' corresponds to 1. This suggested the possibility of the one electron reaction is

$$RSH + Hg \rightarrow RSHg + H^+ + e^-$$

The $E_{1/2}$ values were found to be independent of RSH which is characteristic of the above equation.

Table 4. Relation between diffusion current and 1-4'-chlorophenyl) 4, 4, 6 trimethylpyrimidine-2-thione (4CPPT) concentration.

Curve	Concentration of PT (mM)	Diffusion current* (μA)	I= id/ $C.m^{2/3}t^{1/6}$
A	0.15	0.522	1.539
B	0.30	1.043	1.537
C	0.45	1.568	1.541
D	0.60	2.089	1.540
E	0.75	2.608	1.538
F	0.90	3.130	1.538

*corrected for the residual current. H_2SO_4 concentration = 0.1M, Sensitivity =10x,
Flow rate of mercury=2.52 mg/sec., Temperature=25 ±1°**C,** Drop time = 3.3sec., pH=2.

Adsorption wave: It has been found that the polarograms exhibited a pre-wave due to the adsorption of the anodic reaction product at the electrode surface. The height of the pre-wave increases with the increasing concentration of the respective reagent.

APPLICATIONS

These studies applied for the effect on the anodic reaction. It is strongly adsorbed at the mercury surface, as indicated by a prewave. The anodic wave of the pyrimidines extends over a fairly wide span of potential. The wave remained unaffected and the pre-wave almost disappeared at higher pH values. Both the pyrimidines exhibited irreversible oxidation peak accompanied by prewave, due to the adsorption of these compounds on the electrode surface.

CONCLUSIONS

The pH of the medium was varied using buffers of different pH values in the range of 2.0-12.0. An anodic wave with a characteristic pre-wave was obtained in all the cases. Though the well-defined nature of the wave remained unaffected, the pre-wave almost disappeared at higher pH values. The $E_{1/2}$ shifted towards more negative side with the increasing pH of the medium. Both the pyrimidines exhibited irreversible oxidation peak accompanied by prewave, due to the adsorption of these compounds on the electrode surface. The number of electrons that participated corresponded to “one” in the electrode reaction from Lingane’s equation used.

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