Polarography of Organic Thio Compounds 2-Oxidation of Sodium Penta Methylene-Dithiocarbamate at dme

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The Polarography of sodium pentamethylene-Dithiocarbamate Na(Pidtc) has been studied, in different supporting electrolytes in pH range 6.0 to 11.0. The Na(Pidtc) gave a single, well defined, diffusion controlled, anodic wave over the concentration range 0.2 mM to 1.2 mM. The analysis of this wave indicates a reversible, one electron electrode reaction. The capillary activity is indicated by a negative shift in electrocapillary maximum potential. The effect of Triton X-100 has a special feature as the wave has been found to split into two, after a certain concentration of the surfactant. The second wave is an inhibition wave rather than an adsorption wave as it is not observed in the absence of the surfactant.

Dithiocarbamates are known for their wide range applications both in industry as well as in agriculture and medicine. N-substituted dithiocarbamates are reported as fungicides (1-4) as early as 1956.

The sodium Pentamethylene-dithiocarbamate also known as Sodium piperidine-N-Carbodithioate [Na(Pidtc)] has been found in a variety of applications in addition to as fungicide in pesticidal preperation (5), in hardening of siloxane resigns (6), in electroplating as brightening agent (7), and as a precipitant for Lead in steels and Nickel (8,9). The electrochemical behaviour of Na (Pidtc) along with other series of alkyl dithiocarbamates is indicted by Randle et al. (10,11), using D.C Polarography, cyclic voltametry, chrono amperometry, and normal coulometry. They reported an identical behaviour of diethyl dithiocarbamate and all other series of alkyl substituted dithiocarbamates with two oxidation waves, the first as an adsorption wave and the second as normal wave, with a little mention of Na (Pidtc). It is therefore desired to study Na (Pidtc) in detail at D M E inorder to develope a simple and rapid polarographic method of analysis. The results reported here show only a single anodic wave in three supporting electrolytes studied in the pH range 6.0 to 11.0.

EXPERIMENTAL

The Sodium pentamethylen-dithiocarbamate was prepared by well established methods (12,13) and recrystallized thrice from benzene. Once recrystallized, Na (Pidtc) was found to be white in colour, and the stock solution is stable for more than a weak.

All the supporting electrolyte solutions were prepared from analytically pure grade chemicals. Double distilled water was used in all experiments. Mercury used in these experiments was double distilled.

Current-voltage curves were measured at 25.0 + 0.1° with a recording Elico type polarograph. All potentials were measured against the saturated calomel electrode (SCE). The solution in the polarographic cell was deaerated by passing pure nitrogen. All experiments were conducted in aqueous medium. The surfactant used was Triton X-100, (Lab. Chem. Industry, Bombay).

Elico pH meter model LI-10 has been used in pH measurements. pH of the solution was noted both at the end and beginning of the reaction in every experiment and found no change.

The characteristics of the capillary used were m = 2.15 mg/Sec., t = 4.14 sec. at a mercury height of 17.3 cm.

RESULTS AND DISCUSSION

D.C. polarograms of sodium pentamethylene-Dithiocarbamate, Na(Pidtc) at DME in various supporting electrolytes (0.1M Na_2HPO_4 - $NaNO_3$, 0.1M NH_4OAC - NH_4OH, and 0.1M boric acid - KNO_3) have the same appearence. In all the supporting electrolytes studied, 1.0 mM Na(Pidtc) gave a single, well defined anodic wave (Fig. 1)

EFFECT OF pH

The effect of pH on 1.0 mM Na(Pidtc) in all supporting electrolytes was studied in the pH range 6.0 to 11.0. Below pH 6.0 or in acidic medium, the wave was found to disappear. This may be due to the decomposition of the compound. It is found that variation of pH has no influence on the half-wave potential and wave height of Na(Pidtc) in all supporting electrolytes

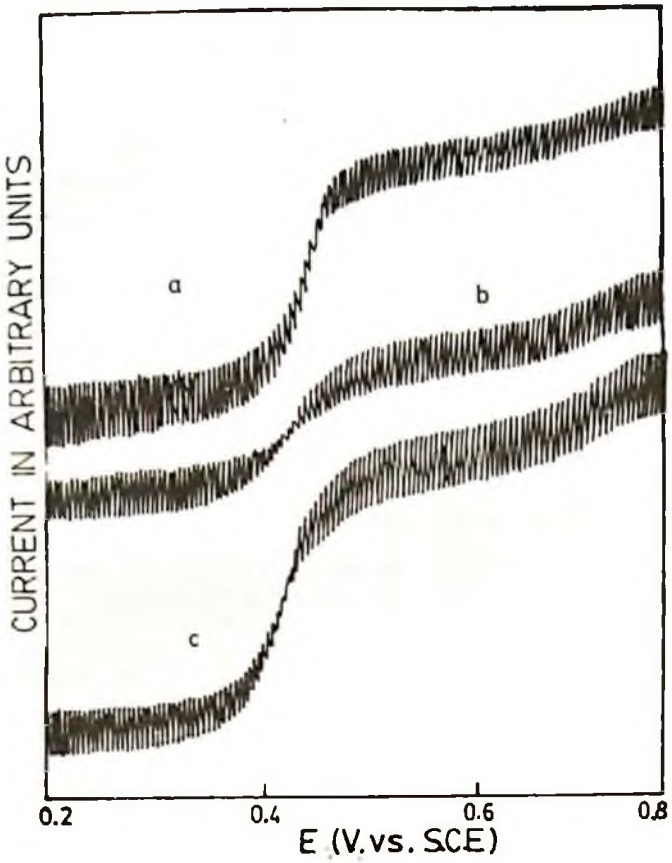


Fig. 1 Typical polarograms of 1.0 mM Na(pidtc)

a:0.1M NH_4OAC +0.1M Na NO_3 pH 9.0
b:0.1M NH_4OAC +0.1M NH_4OH pH 8.0
c:0.1M Boric acid + 0.1M KNO_3 pH 7.0

(Table 1). The results indicate that the kinetics of the electrode reaction is independent of pH and no proton involvement in the electrode reaction.

TABLE 1

EFFECT OF pH ON Na(Pidtc) IN DIFFERENT SUPPORTING ELECTROLYTES-CONCENTRATION OF Na(Pidtc) : 1.0mM

Mercury Height : 23.6 cm
Sensitivity : 0.1μA/mm.

pH	$E_{1/2}$ vs SCE		
	a	b	c
7.0	0.460	0.450	0.445
8.0	0.460	0.450	0.450
9.0	0.459	0.450	0.450
10.0	0.460	0.460	0.450
11.0	0.460	-	0.450

a) 0.1 M Na_2HPO_4 + $NaNO_3$
b) 0.1 M NH_4OAC + NH_4OH
c) 0.1 M Boric Acid + KNO_3

EFFECT OF SUPPORTING ELECTROLYTE CONCENTRATION

Effect of change in supporting electrolyte concentration from 0.05M to 1.0M on 1.0mM Na(Pidtc) has been studied in all supporting electrolytes at pH~ 8.0 and found that the ionic strength has no effect on the nature and height of the wave.

EFFECT OF MERCURY PRESSURE

The effect of change in mercury height on (1) polarograms of 1.0 mM Na(Pidtc) in all three supporting electrolytes (0.1M) at all pHs was studied and the value $id/\sqrt{h}$ was found to be constant. This evidently indicates that the wave height of Na(Pidtc) was controlled purely by the rate of diffusion of the electroactive species to the electrode. Details of these results are given in Table 2.

TABLE 2

EFFECT OF MERCURY PRESSURE ON Na(Pidtc) IN DIFFERENT SUPPORTING ELECTROLYTES

Concentration of Na(Pidtc) = 1.0 mM
Sensitivity : 0.1 μA/mm
Temperature = 25 ± 0.1°C

Mercury Height	id (μA)			$id/\sqrt{h}$		
(cm)	a	b	c	a	b	c
23.6	5.0	3.25	4.63	1.029	0.669	0.95
28.4	5.5	3.5	5.06	1.032	0.656	0.95
33.3	5.875	3.81	3.5	1.018	0.659	0.95
38.3	6.25	4.1	5.88	1.009	0.660	0.95
43.3	6.625	4.37	6.25	1.007	0.664	0.95

a) 0.1M Phosphate, $NaNO_3$ pH~9.5
b) 0.1M NH_4OAC, NH_4OH pH~8.0
c) 0.1M Borate, KNO_3 pH~7.0

EFFECT OF TEMPERATURE

A temperature variation from 25° to 52°C on 1.0mM Na(Pidtc) in 0.1M ammonium acetate, NH_4 OH supporting electraolyte at pH 9.0 has little effect on the shape of the polarograms. The limiting current of 1.0mM Na(Pidtc) has been increased by 1.3% per degree raise of temperature, which also indicates diffusion controlled nature of the wave. A similar behaviour is observed in all the supporting electrolytes.

EFFECT OF TRITON X-100

Effect of surface active substance like TRX-100 on the polarograms of Na(Pidtc) was studied upto

0.04% in all the supporting electrolytes. This has no influence on the shape and height of the wave upto a concentration of 0.002%. But above this concentration the single wave splitted into two. The total wave height remained constant upto 0.008% TRX-100. Above this, the limiting current started decreasing with well seperated, highly reversible two waves.

The development of the second wave in the presence of higher concentrations of TRX-100 (0.002% to 0.04%) may be due to inhibition of the current rather than adsorption, as there is no adsorption wave in the absence of TRX-100. The inhibition may have been caused by a surface film of the electrode reaction product on the mercury drop in presence of TRX-100, or the surfactant itself contributing to restrict the passage of electro-active species at the electrode.

ELECTRO CAPILLARY CURVES

Capillary activity of Na(Pidtc) was markedly represented from the change in drop time of mercury as is evident from the electrocpillary curves obtained in 0.1M borate KNO_3 supporting electrolyte at pH $\sim$ 8.0 (Fig. 2). The electrocapillary maximum is shifted from -0.8 V to -1.0 V in aqueous medium and no shift in alcohol medium are observed. The discontinuity of electro capillary curve on both the positive and negative side of the half-wave potential indicates the electro active nature of the compound.

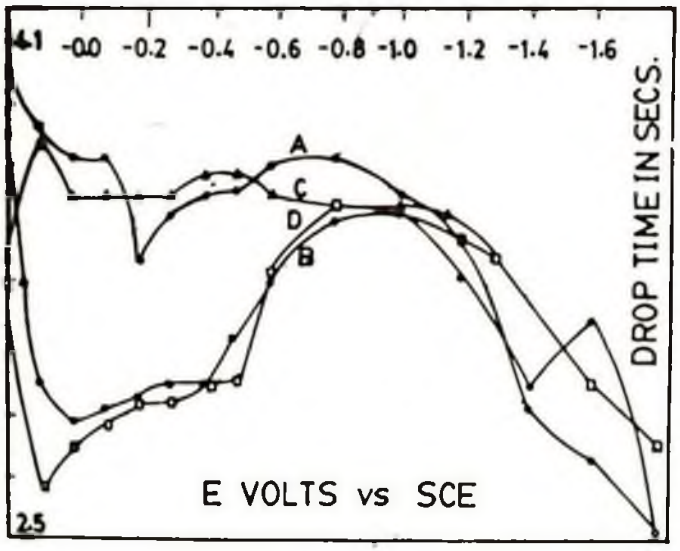


Fig. 2 Electrocapillary Curves at pH$\sim$ 9.0
A -0.05M Boric acid+0.1M Potassium Nitrate +0.001% TRX-100
B -Composition of A+1mM Na(pidtc)
C -Composition of A+50% Alcohol
D -Compositon of C+1mM Na(pidtc)

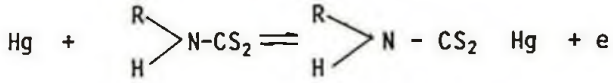
EFFECT OF CONCENTRATION OF Na(Pidtc)

The relation between the wave height and Na(Pidtc) concentration was studied in detail in all the three supporting electroyltes of concentration 0.1M and at all pHs. The diffusion current is proportional to concentration between 0.2 mM to 1.2 mM Na(Pidtc) which also indicates the diffusion controlled nature of the wave. The fungicide therefore may be analyzed to a minimum concentration of 0.2 mM.

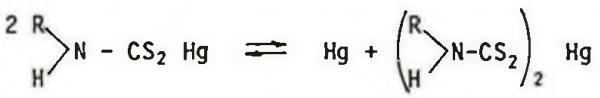
ALALYSIS OF THE WAVE

The plot of log $[i/id-i]$ vs E is a straight line with a slope of 0.060 in 0.1M boric acid, KNO_3 supporting electrolyte of pH $\sim$ 9.0. The slope values indicate only one electron involvement in the oxidation of Na(Pidtc).

Thus in aqueous solution the polarography of Na(Pidtc) involves one electron oxidation.



Which rapidly disproportionates to form $\overline{Hg\ (Pidtc)_2}$



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