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Adsorption studies of potassium heptyl xanthate at mercury electrode surface

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ABSTRACT

Polarographic studies of potassium heptyl xanthate (Khxan) at dropping mercury electrode reveals that the product of anodic reaction is strongly adsorbed at the mercury surface as indicated by a prewave. The anodic wave of xanthate (adsorption and diffusion together) extends over a wide span of potential + 0.2 to - 0.5 V vs SCE. The current of total wave is proportional to the concentration of xanthate from 0.30 to 1.20 mM. The experimental conditions developed are extended for its analysis in spiked water samples as xanthates belong to miscellaneous pesticide class.

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KEYWORDS

D.C. Polarography;
Cyclic voltammetry;
Potassium heptyl xanthate.

INTRODUCTION

Xanthates belong to miscellaneous class of pesticides and therefore their analysis by simple, rapid and specific polarographic method is important. The oxidizing property of xanthates at mercury electrode is due to the presence of -SH group has not been explored much^[1-9]. Few simple xanthates have been studied earlier in these laboratories for their oxidizing^[10-13] and catalytic properties^[14-33] by polarographic and cyclic voltammetric techniques at mercury electrode. The voltammetric investigations of potassium heptyl xanthate (Khxan) at mercury electrode are now reported here.

EXPERIMENTAL

Khxan was prepared according to the method described by Keskyula^[34]. The supporting electrolyte,

boric acid is prepared from pure sample (E.M).

The equipment used is polarographic model CL-357 coupled with LX-300+ EPSON type printer manufactured by Elico pvt Ltd (India). Cyclic voltammograms are recorded using a voltammograph Model CV-27 coupled with an R-XY recorder manufactured by BAS, USA. pH measurements are made by using pH meter, model LI-120(Elico Private Limited) with glass electrode of pH range 0-13.. The potential values mentioned here are referred to SCE.

RESULTS AND DISCUSSION

D.C. Polarography

At pH lower than 4.0 Khxan decomposes into its components. Current – potential curves at DME are therefore obtained with solutions from pH 5.0 to 9.0 in different buffers (ammonium tartrate, ammonium chlo-

ride, and Boric acid) and found to have same appearance. All polarograms exhibit a characteristic pre wave at the negative side of the main wave (Figure 1). 0.2M boric acid at pH 8.0 is used for all studies. The anodic wave of xanthate (adsorption and diffusion together) extends over a wide span of Potential +0.2 to -0.5 V Vs SCE. The height of pre-wave remains constant at concentration equal to or larger than 0.3 mM of Khxan. The limiting current of xanthate is not proportional to the concentration in the entire concentration range investigated (0.10 to 1.2mM) and the values of i/c increases with increasing concentration. However, the proportionality between the current and concentration is seen from 0.30 to 1.2 mM the current below 0.30 mM of xanthate is only due to adsorption of the oxidation product of xanthate over mercury which may be used for the quantitative analysis of xanthate. At various heights of the mercury column the ratio of i/\sqrt{h} is constant with the diffusion current of the total wave. The height of the pre-wave is also proportional to the length of the mercury column till its height remained constant. Temperature variation from 293 to 393 K has a little effect on the polarogram. Experiments performed with varying concentration of gelatin indicate that suppressor has no effect on the polarograms of xanthate.

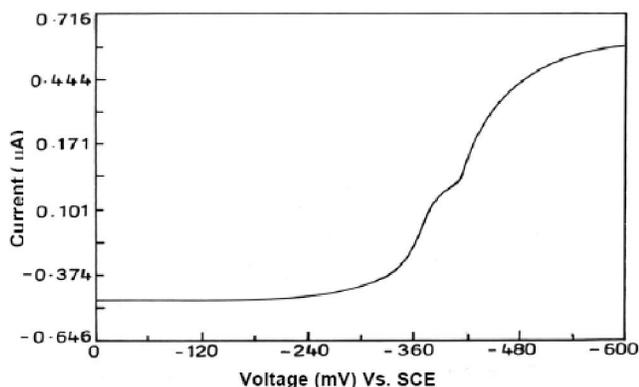
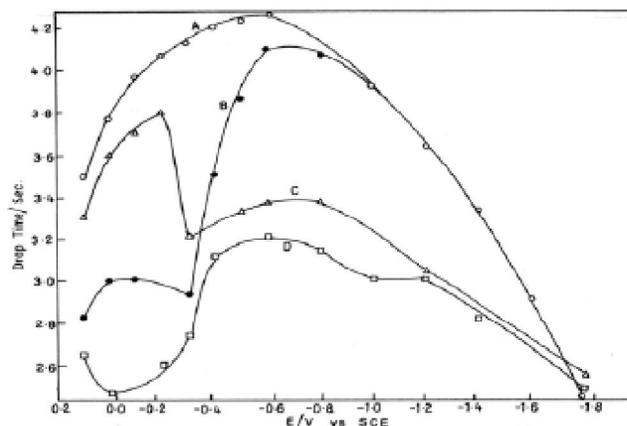


Figure 1 : Typical polarogram of Khxan in 0.2 M boric acid, pH ~ 8.0

Electrocapillary curves

Electrocapillary curves of Khxan at pH 8.0 in 0.2 M boric acid show a marked decrease in the drop time at DME (Figure 2). The depression occurs in a potential range where the adsorption wave is observed and the electrocapillary maximum shifted to negative potentials indicating adsorption of the product of anodic reaction. Presence of alcohol suppressed the surface

tension at the mercury drop (curve c). The large effect on the surface tension due to xanthates (curve d) indicates that the reaction product is strongly adsorbed to give pre-wave.

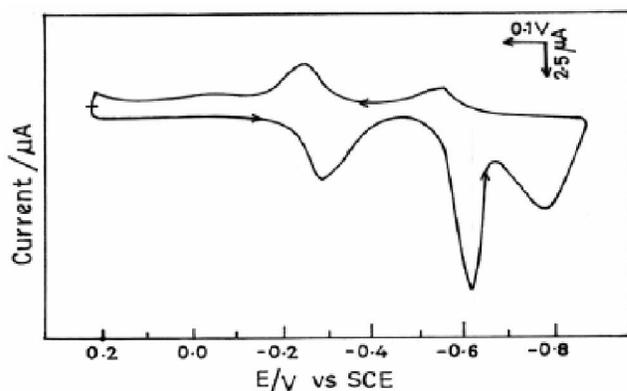


- A. 0.2 M Boric acid
- B. Composition of A + 1.0 mM Khxan
- C. Composition of A + 50% alcohol
- D. Composition of C + 1.0 mM Khxan

Figure 2 : Electrocapillary curves of Khxan at pH ~ 8.0

Voltammetry of Khxan

Typical cyclic voltammogram of Khxan in 0.2 M boric acid supporting electrolyte at pH 8.0 is shown in Figure 3. On the anodic scan two peaks are observed corresponding to d.c polarographic adsorption and normal waves. The peak E_{pa} (I) at negative potential (-0.56) corresponding to the adsorption prewave (wave -1) of d.c polarogram and the peak at -0.25 v E_{pa} (II) represents the normal diffusion wave (wave-II) of d.c polarography.



- pH : ~ 8.0
- Khxan : 1.0 mM
- Scan rate : 0.2 V S⁻¹

Figure 3 : Typical cyclic voltammogram of Khxan in 0.2 M boric acid

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Both the prepeak and normal diffusion peak show corresponding peaks $E_{p,c}$ (I) and $E_{p,c}$ (II) in the cathodic sweep indicating reversible nature of the processes.

At very low concentration of xanthate only one peak is observed due to adsorption at a fixed scan rate. As the concentration is increased adsorption as well as diffusion process in the form of two peak currents, $I_{p,a}$ (I) and $I_{p,a}$ (II) are observed. Reverse scan shows a response related to $i_{p,a}$ (I) the shapes of which is symmetrical at the peak potential but the peak height is much more than the anodic scan. $I_{p,a}$ (I)/ $I_{p,a}$ (II) is less than unity at low scan rates and increases with increase in scan rate indicating strong adsorption of the product. In addition, the peak potential difference, $E_{p,a}$ (I) - $E_{p,a}$ (II) is more than 270 mV confirming strong adsorption of the product. $I_{p,a}$ (I) is also proportional to square root of v at low scan rates. However, at high scan rates the current function $I_{p,a}/\sqrt{v}$ increased with increase in scan rate. A slight decrease in diffusion peak current function, $I_{p,a}$ (II)/ \sqrt{v} is observed due to depletion of material near the electrode surface. The ratio, $I_{p,a}$ (I)/ $I_{p,a}$ (II) is unity at low scan rates suggesting reversible electrode process involving one electron in the process. The results are shown in TABLES 1 and 2.

TABLE 1 : Effect of concentration

Supporting electrolyte: 0.2 M boric acid
Scan rate: 0.2 vs⁻¹ pH: ~8.0

Khxan conc mM	$E_{p,a}$ (II) -V vs SCE	$I_{p,a}$ (II) μ A	$I_{p,a}$ (II)/C μ A/mM	$E_{p,a}$ (I) -V vs SCE	$I_{p,a}$ (I) μ A	$I_{p,a}$ (I)/C μ A/mM
0.06	-	-	-	0.66	1.50	25.0
0.08	0.270	0.60	7.50	0.66	2.00	25.0
0.10	0.265	1.10	11.00	0.66	2.50	25.0
0.20	0.260	2.75	13.75	0.66	2.50	12.5

TABLE 2 : Effect of scan rate

Boric acid : 0.2 M Khxan: 1.0 mM pH: ~ 8.0

Scan rate Vs ⁻¹	$E_{p,a}$ (II) -V vs SCE	$I_{p,a}$ (II) μ A	$I_{p,a}$ (II)* V ^{1/2}	$E_{p,c}$ (II) -V vs SCE	$I_{p,c}$ (II) μ A	$E_{p,a}$ (I) -V vs SCE	$I_{p,a}$ (I) μ A	$I_{p,a}$ (I)* V ^{1/2}	$I_{p,a}$ (I) (II)
0.02	0.27	1.650	11.78	0.325	1.75	0.660	0.50	3.60	0.30
0.04	0.27	2.275	11.45	0.330	2.40	0.660	0.75	3.75	0.32
0.06	0.27	2.600	10.85	0.330	2.75	0.660	1.20	5.00	0.46
0.08	0.26	3.000	10.75	0.350	3.25	0.665	1.85	6.60	0.61
0.10	0.26	3.400	10.67	0.320	3.60	0.660	2.50	7.80	0.73
0.20	0.25	4.400	10.00	0.310	4.50	0.665	3.50	8.00	0.79
0.40	0.24	6.100	9.75	0.300	6.25	0.650	5.50	8.70	0.90

Applications

Determination of Khxan in spiked water sample

100 ml of the water sample (tap water) is spiked with known concentration of xanthate. Aliquot of the solution is taken into the polarographic cell maintaining optimum conditions and made up to 50 ml and polarographed. The amount of xanthate is determined from the calibration graph

TABLE 3 : Determination of Khxan in spiked water samples

S.No	Amount taken, ppm	Amount found, *ppm	Recovery, %	Standard Deviation
1	45.00	44.00	97.70	0.07
2	48.44	47.45	97.90	0.09
3	55.36	54.50	98.40	0.08
4	60.55	59.65	98.40	0.10

*Average of Six determinations.

CONCLUSIONS

The Khxan oxidizes reversibly at mercury electrode as indicated from the D.C polarographic results and E_{pa} (II) - E_{pc} (II) values of cyclic voltammetry. The number of electrons participated corresponded to one in the electrode reaction both from Lingane equation used and from E_{pa} (II) - E_{pc} (II) values. The electrode reaction product is found to adsorb strongly on the mercury electrode from the observations recorded in the electrocapillary curves and E_{pa} (I) and E_{pa} (II) values.

The oxidation of Khxan at mercury electrode may therefore be written as



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