INTRODUCTION

Since the discovery of polarography by Heyrovski it has been extensively employed for qualitative detection and quantitative analysis of electro-oxidisable or reducible substances. In recent years, it has proved to be an efficient method for investigation of oxidation-reduction equilibria, keto-enolic tautomerism, etc., of a number of organic substances. Thus Sartori and Liberti\(^1\) studied the oxidation-reduction of alloxan-dialuric acid; and Smith and Waller\(^2\) examined the equilibrium of nitrosobenzene-N-phenyl-hydroxylamine. Muller and Baumberger\(^3\) investigated the keto-enolic equilibrium of quinol and benzoquinone system. Polarographic technique is also found to be very useful in understanding the electro-chemical oxidation and reduction mechanism especially the number of electrons involved therein and the reversible or irreversible nature thereof. The reduction of formaldehyde at the dropping mercury electrode was found to take place according to the following mechanism\(^4\):

\[
\text{HCHO} + 2e^+ + 2H^+ \rightarrow \text{CH}_3\text{OH}
\]

Distinction between reversible and irreversible organic reductions is also brought out from polarographic analysis. In a reversible oxidation-reduction system, the half-wave potential for the oxidation of the reductant is identical with that for the reduction of the oxidant; and is equal to the potentiometrically determined normal potential of the system.\(^5\)\(^6\) The two, reversible and irreversible, processes are controlled by equations involving different and characteristic quantities (vide infra).

The present investigation deals with polarographic studies of murexide or ammonium salt of purpuric acid.
This substance has been widely used as an indicator for metal ions, especially of Ca$^{++}$. Thus Beck$^9$ employed murexide as an analytical reagent for Sc, Zn, Th and other rare earth metals; Engel$^{10}$ used the same for titrimetric determination of Ca$^{++}$ and Mg$^{++}$. And, Oestertag and Rinck$^{11}$ studied the colorometric estimation of Ca$^{++}$ with the aid of murexide. Smeets and Seekles$^{12}$ determined spectrophotometrically the content of Ca$^{++}$ in milk-ultrafiltrate. Murexide was also employed for analytical work in pharmaceutical and textile products. During a series of trials for estimation with murexide of the calcium content in sugarcane juices, it appeared desirable to investigate in detail the polarography of murexide, the knowledge of which would be of utility for development of ampereometric titrations with murexide.

**EXPERIMENTAL**

The commercial (B.D.H.) sample of murexide was purified according to the method described by Davidson$^{15}$; this method was found to give 99–100% purity.$^{16}$ One gram of the substance was dissolved in 900 c.c. of pure twice distilled water and the filtered solution was salted out with ammonium chloride. The precipitated substance was washed several times with absolute methyl alcohol and later dried at 120°C.

0.1 N potassium chloride (Analar quality) solution was used as the supporting electrolyte. The dissolved air in the solutions was removed by bubbling purified nitrogen. 0.5% of gelatin was used as the maximum suppressor.*

The polarograms at different concentrations of murexide were obtained by a manual polarograph set up in this Laboratory. The following were the characteristics of the capillary of the dropping mercury electrode in 0.1 N potassium chloride solution with open circuit:

- Mass of the drop = 3.23 mg.
- Drop time = 1.64 sec.

A pool of mercury at the bottom of a cell (capacity 100 ml.) served as the other electrode. D.C. potentials obtained from a potentiometer and applied to the dropping mercury electrode (used as cathode in this investigation) and mercury pool, could be read accurately up to 1 millivolt. The current flowing through the system was measured as follows: A suitable carbon resistor was introduced serially into the circuit; the potential developed across the same due to the passage of the current was measured by a Leeds and Northrup

* Murexide exhibits a pronounced positive maximum; the details of the effect of maximum suppressors like gelatin, methyl red, etc., will be reported in a later communication.