

# POLAROGRAPHIC STUDIES OF MUREXIDE—I

BY N. A. RAMAIAH AND VISHNU

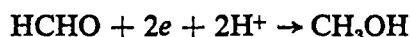
(Department of Physical Chemistry, Indian Institute of Sugar Technology, Kanpur)

Received March 9, 1956

(Communicated by K. S. G. Doss, F.A.Sc.)

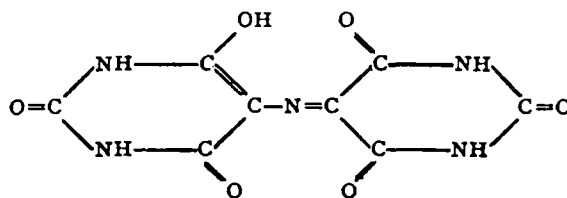
## INTRODUCTION

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<sup>1</sup> studied the oxidation-reduction of alloxan-dialuric acid; and Smith and Waller<sup>2</sup> examined the equilibrium of nitrosobenzene-N-phenylhydroxylamine. Muller and Baumberger<sup>3</sup> 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<sup>4</sup>:



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.<sup>5, 6</sup> 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  $\text{Ca}^{++}$ .<sup>7, 8</sup> Thus Beck<sup>9</sup> employed murexide as an analytical reagent for Sc, Zn, Th and other rare earth metals; Engel<sup>10</sup> used the same for titrimetric determination of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ . And, Oestertag and Rinck<sup>11</sup> studied the colorometric estimation of  $\text{Ca}^{++}$  with the aid of murexide. Smeets and Seekles<sup>12</sup> determined spectrophotometrically the content of  $\text{Ca}^{++}$  in milk-ultrafiltrate. Murexide was also employed for analytical work in pharmaceutical<sup>13</sup> and textile<sup>14</sup> 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 amperometric titrations with murexide.

#### EXPERIMENTAL

The commercial (B.D.H.) sample of murexide was purified according to the method described by Davidson<sup>15</sup>; this method was found to give 99–100% purity.<sup>16</sup> 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:

$$\text{Mass of the drop} = 3.23 \text{ mg.}$$

$$\text{Drop time} = 1.64 \text{ sec.}$$

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.

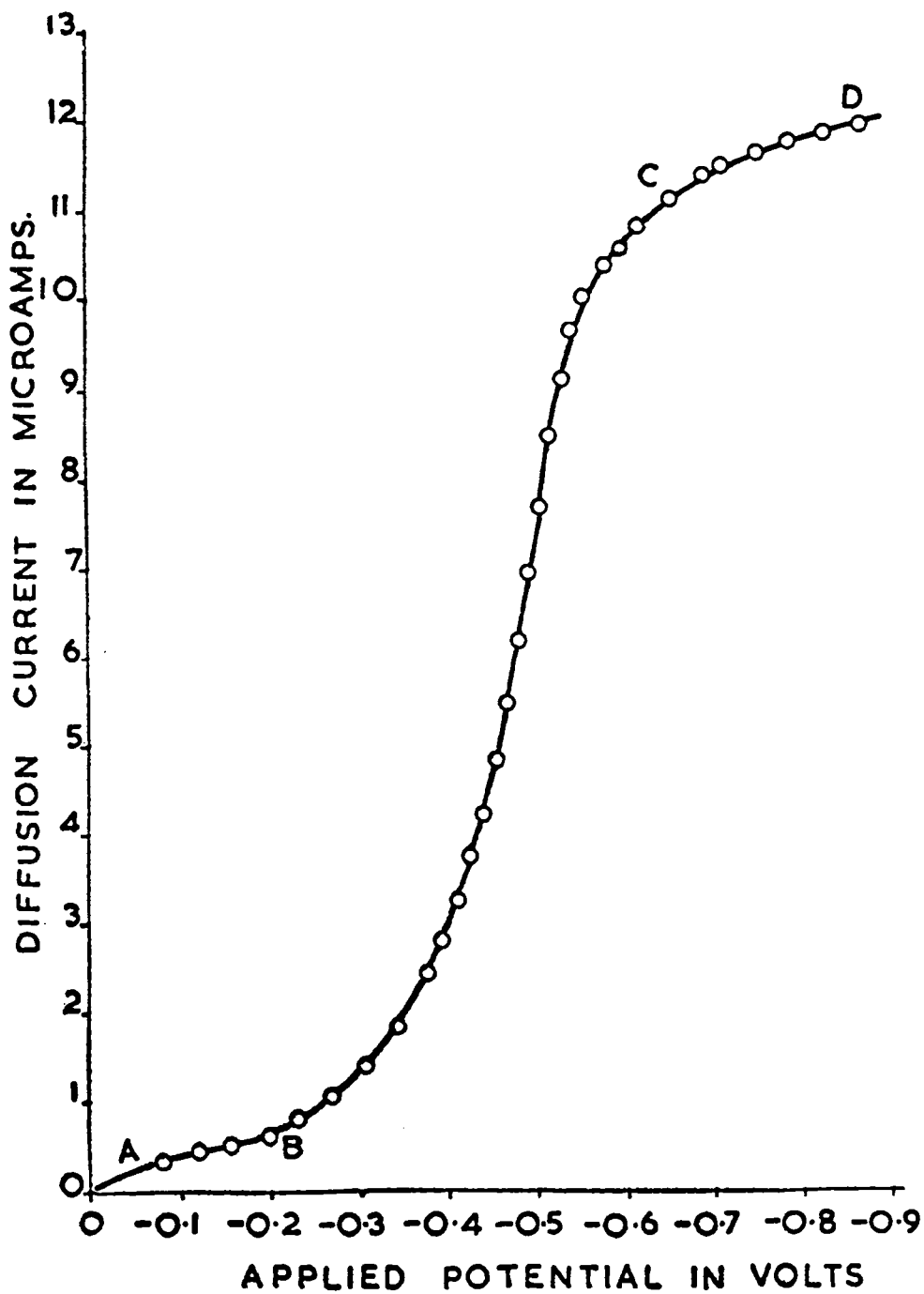


FIG. 1 Polarogram of murexide in 0.1 N KCl solution.

potentiometer; the accuracy of the measurement was 0.5 of a millivolt, which corresponded to 0.05 of a microampere.

#### RESULTS AND DISCUSSION

Figure 1 gives a typical series of results representing the variation of the current  $i$  with potential  $E$  applied to the dropping mercury electrode; the data refer to a concentration of 1.4 mM of murexide (at neutral pH). When the dropping mercury electrode was made progressively negative, at low applied potentials only a minute current could be recorded (AB, Fig. 1). When the potential was increased beyond a characteristic value corresponding to the decomposition potential, marked increase in  $i$ , tending to saturation at large values of  $E$ , was noticed. Examination of the data in Fig. 1 shows clearly that as for the other reducible substances, the results for murexide gave characteristic S-shaped curves usually known as the polarograms. Further, it may be noted that the polarogram was poorly "defined" in the sense that the portions representing the residual current (portion AB) and limiting current (CD, Fig. 1) were not parallel to the voltage-axis, as is to be expected from theoretical considerations. This was primarily due to the low concentrations of murexide employed in the present investigation. Use of larger concentrations met with the difficult circumstance of salting out of the substance by the supporting electrolyte (KCl). At low concentrations, the appreciable rate of change of *condenser* current with the applied voltage led to the observation of progressively increasing limiting currents (Fig. 1). When the residual current was corrected for, well-defined curves could be obtained at all concentrations studied; a few of the typical series of these results are given in Fig. 2. In this, curves 1-4 refer respectively to 0.8, 1.0, 1.2 and 1.4 mM of murexide. It was interesting to note that the diffusion current ( $i_d$ ) decreased progressively with a reduction in the concentration of murexide. Thus, e.g.,  $i_d$  was 10.3, 8.6 and 7.4  $\mu$ amp. at 1.4, 1.2 and 1.0 mM of murexide. With concentration  $C$ ,  $i_d$  increased roughly linearly (see Fig. 3) in accordance with Ilkovic's equation.<sup>6</sup> Further, the half-wave potential ( $E_{1/2}$ ) characteristic of the electro-active substance was -0.38 volts vs. S.C.E. for murexide in 0.1 N KCl solution; it was not sensibly affected by a change in the concentration of the substance (see inset, Fig. 2). These data indicate clearly that murexide is reducible at the dropping mercury electrode.

Kuhn and Lyman<sup>17</sup> investigated the reduction of murexide with  $\text{Na}_2\text{S}_2\text{O}_4$  and observed that reduction of one molecule of murexide required 2 atoms of H, leading to the production of a leuco-compound.

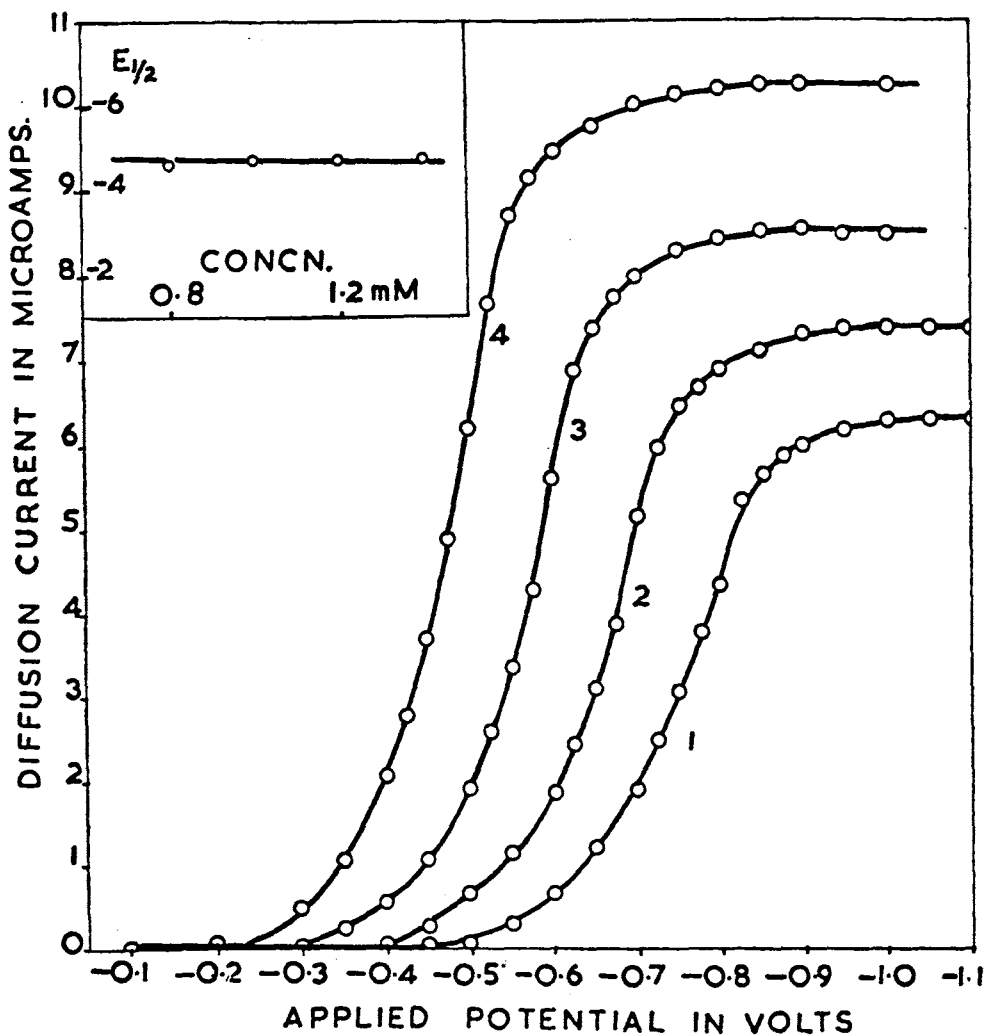


FIG. 2. Reduction of murexide at the dropping mercury electrode, at different concentrations. The potential scale for curve 4 is marked on the abscissa; the other curves have been shifted progressively to the right by 0.1 volt.

Heyrovsky and Ilkovic<sup>18, 19</sup> deduced the following equations for reversible and irreversible reduction processes occurrent at the dropping mercury electrode:

$$E = E_{\frac{1}{2}} - \frac{0.0591}{n} \log (i/i_d - i) \quad (\text{reversible})$$

$$E = E_{\frac{1}{2}} - \frac{0.0591}{\alpha} \log (i/i_d - i) \quad (\text{irreversible})$$

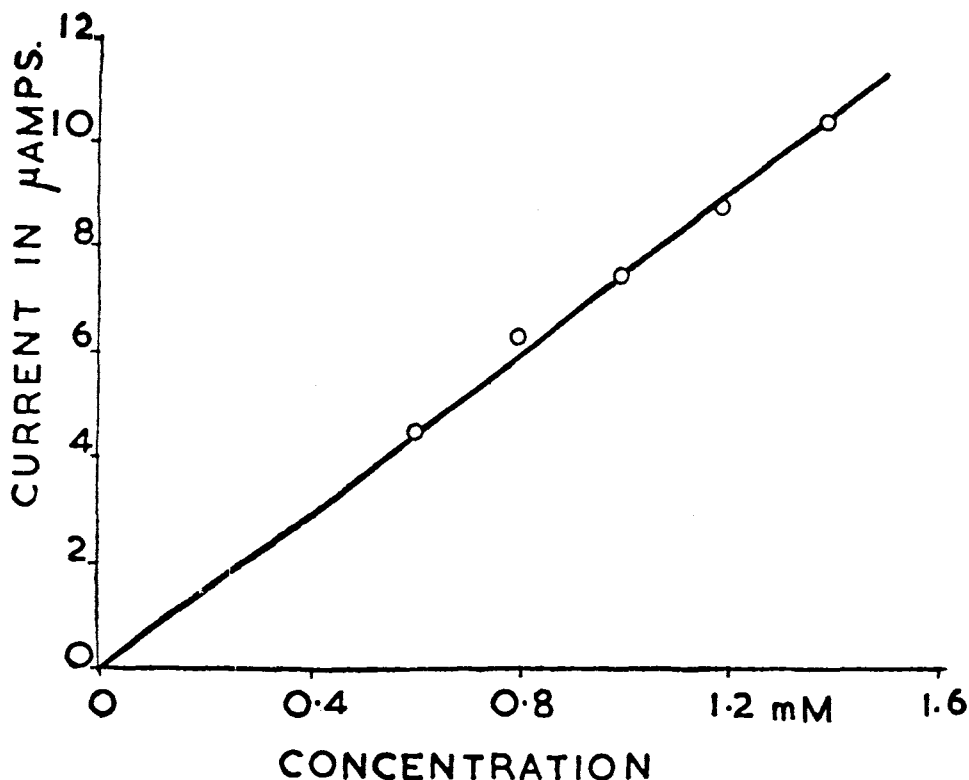


FIG. 3. Effect of concentration on the diffusion current  $i_d$ .

where  $n$  is the number of electrons involved in the reversible reduction process; and  $a$  also contains a factor related to the rate constant of a slow reaction responsible for the irreversible nature of the reduction. In the former equation,  $n$  is always an integer and is equal to or greater than unity while in the equation for irreversible process  $a$  is found very often, though not invariably, to be less than one. Both these equations require that  $E_{\frac{1}{2}}$  should be constant and independent of the concentration of the electroactive substance (*vide supra*); and that the plots  $\log (i/i_d - i)$  vs.  $E$  should be linear. It is instructive to consider from the data in Fig. 4 that for the reduction of murexide at the dropping mercury electrode,  $\log (i/i_d - i)$  varies roughly linearly with applied potential,  $E$ . The slope of the line was, approximately, 0.5 (*cf.* also Table I), leading to the deduction that the reduction of murexide at the dropping mercury electrode is irreversible in nature.

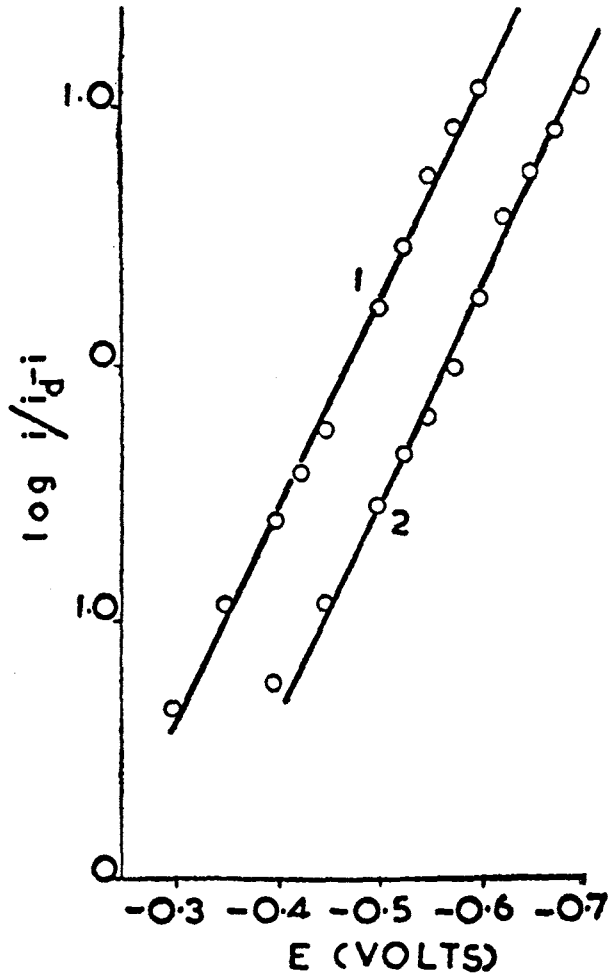


FIG. 4. Variation of  $\log i_p/i_{601}$  with applied potential E.

TABLE I

Applied potential $E$ (volts)	Concentration = 1.4 mM			Concentration = 1.2 mM		
	$i$ ( $\mu$ A)	$\log (i/i_d - i)$	$\alpha$	$i$ ( $\mu$ A)	$\log (i/i_d - i)$	$\alpha$
- 0.300	0.50	- 1.29	0.43	.55	-1.17	0.39
- 0.350	1.05	- 0.94	0.44	1.04	-0.87	0.40
- 0.400	2.05	- 0.60	0.46	1.89	-0.56	0.42
- 0.425	2.80	- 0.43	0.48	2.58	-0.37	0.42
- 0.450	3.68	- 0.26	0.54	3.36	-0.20	0.42
- 0.500	6.46	+ 0.23	0.61	5.62	+0.26	0.70
- 0.525	7.67	0.46	0.58	6.89	0.58	0.73
- 0.550	8.72	0.74	0.60	7.40	0.76	0.62
- 0.600	9.50	1.07	0.52	8.03	1.09	0.52
			Mean 0.52			Mean 0.52

$E_{\frac{1}{2}} = 0.478$  Volts;  $i_d$  for  $C = 1.4$  mM was  $10.30 \mu$ A; and  $i_d$  for  $C = 1.2$  mM was  $8.69 \mu$ A.

## SUMMARY

Reduction of murexide at the dropping mercury electrode was investigated. Data obtained at different concentrations in the range 0.5–2 mM showed that the half-wave potential of murexide was  $-0.38$  volt vs. S.C.E. in 0.1 N KCl solution (neutral pH) and was not altered with concentration; with this last, the diffusion current increased linearly. Analysis of the plots  $\log (i/i_d - i)$  vs.  $E$  indicated that the reduction was irreversible in nature.

## ACKNOWLEDGEMENT

Authors' grateful thanks are due to Professor K. S. G. Doss, D.Sc., F.R.I.C., F.INST.P., F.A.Sc., Director, Indian Institute of Sugar Technology, Kanpur, for his kind interest in the work.

## REFERENCES

1. Sartori, G. and Liberti, A. *Ric. Sci.*, 1946, 16, 313.
2. Smith, J. W. and Waller, J. G. *Trans. Farad. Soc.*, 1950, 46, 290.



3. Muller, O. H. and Baumberger, J. P. *Trans. Electrochem. Soc.*, 1937, **71**, 181.
4. Jahoda, F. G. .. *Coll. Czech. Chem. Comm.*, 1935, **7**, 415.
5. Page, J. E. .. *Quarterly Reviews*, Chemical Society, London, 1952, **6**, 277.
6. Kolthoff, I. M. and Lingane, J. J. *Polarography*, Interscience Publishers, 1952.
7. Kulberg, L. .. *J. Gen. Chem., U.S.S.R.*, 1947, **17**, 1089.
8. Schwarzenbach, G. and Gysling, H. *Helv. Chim. Acta*, 1949, **32**, 1314.
9. Beck, G. .. *Anal. Ghim. Acta*, 1947, **1**, 69.
10. Engel, O. .. *Das Leder*, 1951, **2**, 241.
11. Ostertag, H. and Rinck, M. E. *Chim. Anal.*, 1952, **34**, 108.
12. Smeets, W. Th. G. M. and Seekles, L. *Nature*, 1952, **169**, 802.
13. Flaschka, H. .. *Scientia Pharma.*, 1953, **21**, 126.
14. ————— .. *Textile Rundschau*, 1954, **9**, 77.
15. Davidson, D. .. *J. Amer. Chem. Soc.*, 1936, **58**, 1821.
16. Moser, J. H. and Williams, M. B. *Anal. Chem.*, 1954, **26**, 1167.
17. Kuhn, R. and Lyman, J. C. *Ber.*, 1936, **69 B**, 1547.
18. Heyrovsky, J. and Ilkovic, D. *Coll. Czech. Chem. Comm.*, 1935, **7**, 198.
19. Cf. Ref. 6, p. 195.