

# POLAROGRAPHY OF BISMUTH IN OXALATE AND THIOUREA MEDIA

BY R. SUNDARESAN AND A. K. SUNDARAM, F.A.Sc.

(Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400085)

Received September 4, 1973

## ABSTRACT

The polarography of bismuth in the presence of thiourea and oxalate is discussed. Measurements could not be made in thiourea medium due to the dissolution of mercury. The reduction was irreversible in oxalate medium and the kinetic parameters as well as the stability constant of the predominant species were calculated from the formal potentials measured by amalgam polarography. The mixed complexes were not formed and the reduction was quasi-reversible in the presence of both the ligands.

## INTRODUCTION

NOT much work has been reported on bismuth complexes. Recently, a few workers have investigated some bismuth complexes by potentiometry<sup>1</sup>, spectrophotometry<sup>2,3</sup> and solvent extraction.<sup>4</sup> The reduction of bismuth at the dropping mercury electrode from non-complexing media is not reversible; the standard rate constant for the reduction is  $3 \times 10^{-4}$  cm. sec.<sup>-1</sup> in 1M perchloric acid<sup>5</sup> and  $3 \times 10^{-3}$  cm. sec.<sup>-1</sup> in 1 M nitric acid.<sup>6</sup> The reduction becomes highly reversible in hydrochloric acid<sup>6</sup> due to complexation. This paper reports a polarographic study of bismuth in thiourea and oxalate media.

## EXPERIMENTAL

Measurements were made at  $30 \pm 0.5^\circ$  C on a manual polarograph using a saturated calomel electrode (S.C.E.) as the reference electrode. The dropping mercury electrode had the following characteristics:  $m = 2.03$  mg. sec.<sup>-1</sup> and  $\tau = 3.4$  secs. (in 1.0 M potassium nitrate, open circuit). A Beckman Expandomatic-SS-2 pH meter was used for the measurement of pH. The reported currents were corrected for the residual currents.

The stock solution of bismuth nitrate (B.D.H., AR) was kept at pH  $\sim 1$  to prevent hydrolysis and was standardised by titration with EDTA.

Potassium nitrate (B.D.H., AR), potassium oxalate (Sarabhai Merck, pro analysi) and thiourea (E. Merck, pro analysi) were used without further purification. The pH of the solutions was adjusted with sodium hydroxide.

### RESULTS AND DISCUSSION

Bismuth gave a well-defined and nearly reversible wave in 1.0M potassium nitrate with the half-wave potential at + 0.021 V vs. S.C.E. A hump-like maximum was observed which could be rounded off without affecting the half-wave potential as the use of a maximum suppressor was not desired.

#### *Bismuth-Thiourea System*

In the presence of 0.04 M thiourea, an ill-defined wave was observed which merged with the steep anodic wave due to mercury. Hence no measurement could be made on this system as the bismuth complexes of thiourea were comparatively weaker than the mercury complexes.<sup>3,7,8</sup>

TABLE I

*Half-wave potential data of bismuth in oxalate medium*

$[C_{Bi} = 1.2 \times 10^{-4} M; \mu = 0.5 \text{ (potassium nitrate)}]$

| (OX)<br>M $\times 10^1$ | $E_{1/2}$<br>-V vs. S.C.E. | $i_a$<br>$\mu A$ | Slope<br>mV | $E_f^\circ$<br>-V vs. S.C.E. | $\alpha$ | $k_s \times 10$<br>cm/sec. <sup>5</sup> |
|-------------------------|----------------------------|------------------|-------------|------------------------------|----------|---|
| 0                       | -0.021                     | 1.40             | 22.0        | ..                           | ..       | ..                                      |
| 0.20                    | 0.268                      | 1.38             | ..          | ..                           | ..       | ..                                      |
| 0.32                    | 0.275                      | 1.01             | ..          | ..                           | ..       | ..                                      |
| 0.80                    | 0.302                      | 1.35             | ..          | 0.240                        | 0.45     | 4.9                                     |
| 1.2                     | 0.315                      | 1.27             | 41          | 0.250                        | 0.51     | 3.4                                     |
| 1.6                     | 0.322                      | 1.25             | 42          | 0.257                        | 0.44     | 4.3                                     |
| 2.4                     | 0.334                      | 1.19             | 42          | 0.271                        | 0.45     | 4.9                                     |
| 3.2                     | 0.342                      | 1.13             | 41          | 0.276                        | 0.48     | 3.1                                     |
| 5.0                     | 0.352                      | 1.04             | 42          | ..                           | ..       | ..                                      |

*Bismuth-Oxalate System*

Polarograms of  $1.2 \times 10^{-4}$  M bismuth in potassium nitrate medium were taken in the presence of different concentrations of potassium oxalate at pH 6. The waves were well defined but the reduction was irreversible as indicated by the slope of the log-plots (Table I). It was therefore decided to determine the formal potentials,  $E^{\circ}_f$ , from the composite polarograms

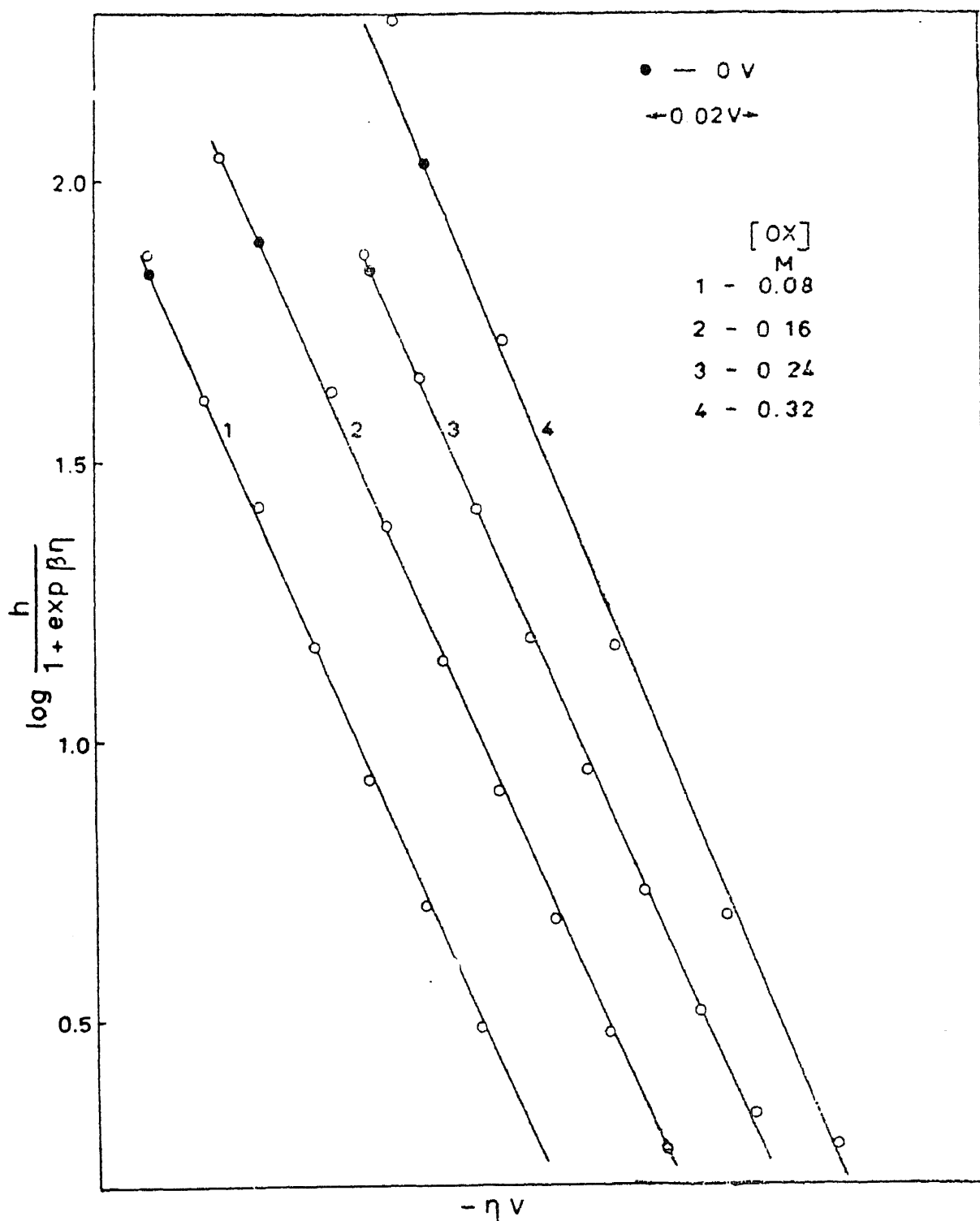


FIG. 1. Plots of  $\log \frac{h}{1 + \exp \beta \eta}$  vs  $\eta$ .

obtained using a dropping bismuth amalgam electrode. The values were obtained<sup>9</sup> from the potential of zero current and the diffusion currents as a function of pA. The kinetic parameters for the reduction, viz., the standard rate constant,  $k_s$  and the transfer coefficient,  $\alpha$ , were obtained by the method described earlier<sup>10</sup> from a plot of  $\log \frac{h}{1 + \exp \beta \eta}$  vs.  $\eta$  (Fig. 1). The reduction is irreversible as seen from the values in Table I. The plot of  $E_f^\circ$  vs. pA was a straight line with a slope of  $-0.06$  V, indicating the predominating species to be  $\text{Bi}(\text{OX})_3$  and the stability constant was calculated as  $2 \times 10^{16}$  using the formal potentials in place of the half-wave potentials in Lingane's equation.<sup>11</sup>

TABLE II

*Polarographic data of bismuth in thiourea-oxalate medium*

| (OX)<br>M | (TU)<br>M | $E_{1/2}$<br>-V vs. S.C.E. | $E_f^\circ$<br>-V vs. S.C.E. | $\alpha$ | $k_s \times 10^4$<br>cm/sec. |
|-----------|-----------|----------------------------|------------------------------|----------|------------------------------|
| 0.04      | 0.04      | 0.222                      | 0.201                        | 0.58     | 2.6                          |
| 0.08      | 0.02      | 0.239                      | 0.222                        | 0.61     | 5.4                          |
| ..        | 0.04      | 0.244                      | 0.224                        | 0.62     | 3.9                          |
| ..        | 0.10      | 0.242                      | 0.225                        | 0.59     | 5.0                          |
| 0.12      | 0.02      | 0.256                      | 0.235                        | 0.59     | 3.5                          |
| ..        | 0.04      | 0.255                      | 0.235                        | 0.60     | 3.9                          |
| 0.16      | 0.04      | 0.270                      | 0.249                        | 0.53     | 4.0                          |
| 0.24      | 0.02      | 0.280                      | 0.258                        | 0.64     | 3.0                          |
| ..        | 0.04      | 0.279                      | 0.260                        | 0.61     | 3.7                          |
| 0.32      | 0.02      | 0.288                      | 0.266                        | 0.62     | 3.2                          |
|           | 0.10      | 0.288                      | 0.268                        | 0.60     | 3.2                          |

### *Bismuth-Thiourea Oxalate System*

An attempt was made to study the mixed complexes of bismuth with thiourea and oxalate. Polarograms of  $1.2 \times 10^{-4}$  M bismuth in potassium

niriate medium were taken in the presence of a constant concentration of thiourea and varying amounts of potassium oxalate at pH 6. The log-plots were curved suggesting the reduction to be quasi-reversible<sup>12</sup> in nature. This was confirmed by the value of  $10^{-4}$  cm. sec.<sup>-1</sup> for the standard rate constant obtained by the analysis of the data by the method of Hale and Parsons<sup>13</sup> (Fig. 2). As seen from Table II, the half-wave potential at an oxalate concentration was constant irrespective of the concentration of thiourea, indicating the absence of formation of mixed complexes. They may probably be formed at lower concentrations of oxalate but no measurements can be made in this region.

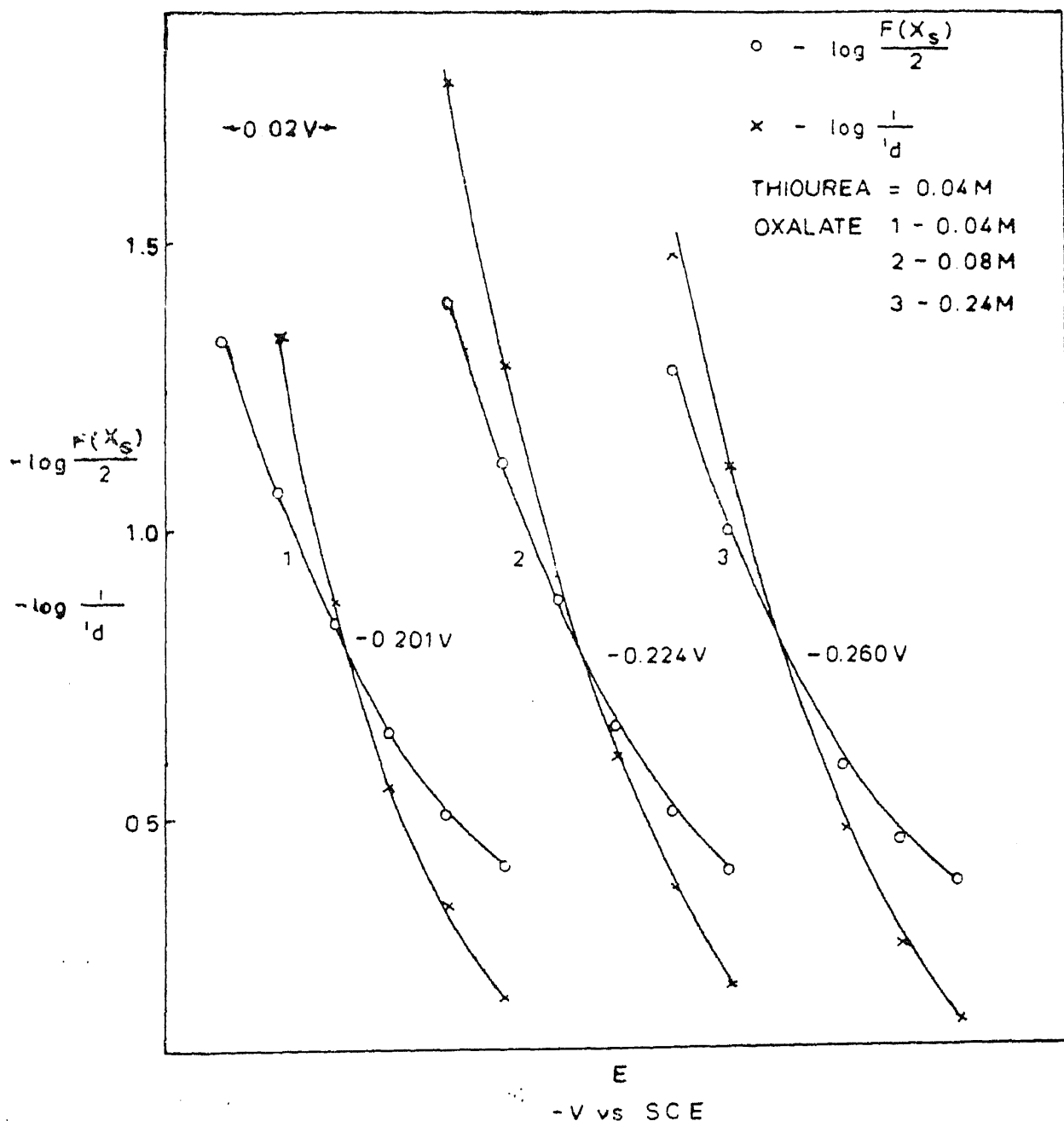


FIG. 2. Method of Hale and Parsons.

In the absence of formation of mixed complexes, the formal potentials obtained in the absence of thiourea and those obtained in its presence should be the same. But the more positive values in the latter case could mean that thiourea, besides accelerating the electrode reaction, also shifts the reduction potentials to more positive values.

#### ACKNOWLEDGEMENTS

The authors wish to thank Dr. M. Sankar Das, Head, Analytical Chemistry Division, for his kind interest.

#### REFERENCES

1. Fedorov, A. V., Kalosh, T. N., Chernikova, G. E. and Mironov, V. E. *Zhur. Fiz. Khim.*, 1971, **45**, 186, 1364.
2. —, — and Mironov, V. E. *Zhur. Neorg. Khim.*, 1971, **16**, 1014.
3. Swaminathan, K. and Irving, H. *J. Inorg. Nuclear Chem.*, 1966, **28**, 171.
4. Stary, J. .. *Anal. Chim. Acta*, 1963, **28**, 132.
5. Kambara, T. and Ishii, T. *Rev. Polarography*, 1961, **9**, 30.
6. Moussa, A. A. and Sammour, H. *J. Chem. Soc.*, 1960, p. 2151.
7. Vasilev, V. P. and Grechina, N. K. *Zhur. Neorg. Khim.*, 1967, **12**, 1567.
8. Nyman, C. J. and Perry, E. P. *Analyt. Chem.*, 1958, **30**, 1255.
9. Milner, G. W. C. .. *Principles and Applications of Polarography*, Longmans Green & Co., 1957.
10. Sundaresan, R. and Sundaram, A. K. *Indian J. Chem.*, 1971, **9**, 148.
11. Lingane, J. J. .. *Chem. Revs.*, 1941, **29**, 1.
12. Koryta, J. .. *Electrochim. Acta*, 1962, **6**, 67.
13. Hale, J. M. and Parsons, R. *Collection Czechoslov. Chem. Commun.*, 1962, **27** 2444.