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MONSANTO CHEMICAL COMPANY - UNIT III

DAYTON, OHIO

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Authority of Paul B. Bond, At 63340
by Albert J. Weidner, 7/14/70
Reviewed by C.W. Huntington 8/21/79

M. M. Haring
Laboratory Director

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PRODUCTION ELECTROLYSIS STUDIES V

(Information Report)

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~~SECRET~~INTRODUCTION

A request was received¹ to determine the decomposition potential of bismuth in nitric acid solution in similar concentrations to those used in production solutions (5 gm. bismuth/L, or 0.024 N bismuth, and 1.5 N nitric acid). This involves a simple polarographic technique uncomplicated by the presence of activity. If activity were present, it would be difficult or impossible to differentiate between reduction currents of solvent decomposition products due to alpha bombardment and reduction currents due to bismuth.

PREVIOUS KNOWLEDGE

Haring² reported a decomposition potential of -0.05 to S.C.E. of 0.01 M bismuth in 1.5 N nitric acid. Using Swift's³ reaction for the bismuth-bismuthyl couple, the decomposition potential for 0.024 M bismuth solution can be calculated as follows:

$$E_1 - E_2 = \frac{.059}{3} \log \frac{a_2^2 \text{H}^+ a_2 \text{BiO}^+}{a_1^2 \text{H}^+ a_1 \text{BiO}^+}$$

$$\text{since } a_1 \text{H}^+ = a_2 \text{H}^+,$$

$$E_1 - E_2 = .020 \log \frac{.024}{.01} = .008.$$

Decomposition potential of .025 M bismuth in 1.5 N nitric acid = $-0.05 - .03 + .01 = -0.07$ to N.C.E.

Page and Robinson⁴ have determined bismuth polarographically in 1 N nitric acid. They report a half-wave of -0.03 volts to S.C.E. (-0.07 volts to N.C.E.). Half-wave potentials are independent of concentration and are more negative than reduction potentials, but they may be compared with half-wave potentials to be determined in this study.

METHOD

The cathode controlled polarograph using platinum electrodes was used as previously described.⁵ A platinum cathode was selected rather than the conventional dropping mercury electrode because of the

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use of platinum cathodes in production. Solutions were swept with nitrogen for 30 minutes before analysis to eliminate oxygen waves. Polarograph cells were immersed in a constant temperature water bath at 25°C. Stirring motors, nitrogen, water, and heater connections were shut off when making a run to minimize vibration.

Bismuth solutions were prepared by dissolving bismuth trioxide in 1.5 N nitric acid.

RESULTS

Decomposition potentials, diffusion currents, and half-wave potentials of bismuth reduction are given in Table I.

Table I

POLAROGRAMS OF BISMUTH SOLUTIONS IN 1.5 N HNO₃ WITH PLATINUM ELECTRODES

Bismuth Concentration		Decomposition Potential vs. N.C.E. Volts	Half-Wave Potential vs. N.C.E. Volts	Diffusion Current Microamps.	Ratio Conc.
gm. Bi ₂ O ₃ per Liter	Molar				
11.148	0.048	-0.06	-0.065	610	2.00 2.14
5.574	0.024	-0.06	-0.065	300	
2.787	0.012	-0.08	-0.09	138	2.00 2.18

Reasonable values for diffusion current ratios give weight to the selection of the current inflections as being due to bismuth reduction (rather than due to the reduction of possible impurities).

The decomposition potential of -0.06 volts for 0.024 M bismuth checks well with the value of -0.07 volts, calculated from Haring's² data, and the half-wave potential checks Page and Robinson's value of -0.07.

According to the Nernst relation, a two-fold decrease in concentration should shift the reversible potential six millivolts negatively. The precision to be expected for the above method is in the order of 5 millivolts, so the decomposition potentials may be following the theoretical relation for equilibrium potentials.

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Half-wave potentials of reversible polarographic waves are independent of concentration. The shifting of the half-wave potentials reported above indicated that the waves were not reversible.

CONCLUSION

Decomposition potentials reported here substantiate the conclusion that bismuth will not be reduced at 25°C. under normal plating conditions (0.00 to N.C.E.) from 1.5 N nitric acid solutions with a bismuth content of 5 grams per liter. A decomposition potential of -0.06 volts to the normal calomel electrode was obtained for this solution.

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