



POLAROGRAPHIC REDUCTION OF IODATE-STUDY OF KINETIC WAVE

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ABSTRACT

Polarographic reduction of the conjugate bases of many halogen oxy acids has been of great importance from the kinetic currents owing to their analytical applications. Many of them have been used as catalytic agents for the reductions of many transition metal ions. The polarographic reduction of Iodate has been investigated in the Acetic acid-Sodium acetate buffer solutions of different pH. A single six electron reduction of Iodate has been reported in the literature. In the present investigations a second wave corresponding to two electron reduction has been reported at 1.62V against SCE. The various studies on the second wave of Iodate and the possible mechanism for it is discussed in the present paper.

Keywords: D.C.Polarography, Iodate, Acetic acid –Sodium acetate buffer, d.m.e, height of the mercury column, kinetic wave, SCE.

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INTRODUCTION

The polarographic reduction of Iodate ion at the d.m.e. was investigated by Rylich¹ in a detailed fashion. He concluded that the total diffusion current corresponds to the following net electrode reaction.



Kolthoff and Orlemann² made a more exact investigation and confirmed that the number of electrons involved in the reduction of Iodate is equal to 6. Rylich made a systematic study on the reduction of Iodate in acid, neutral and alkaline unbuffered solutions. Kolthoff and Orlemann obtained two waves of 1 and 5 electron reduction in dilute solutions of strong acids when the hydrogen ion concentration is smaller than two times the concentration of Iodate. The authors of the present investigation report the presence of two waves of 6 and 2 electron reduction in buffer solutions of certain anions capable of forming complex with Iodate cation.

EXPERIMENTAL

Reagents

All chemicals used were of analytical-reagent grade. Potassium iodate solution (0.1M) prepared in conductivity water with appropriate response is used. A 0.2 M Sodium acetate and acetic acid buffer solutions of different pH have been employed in the investigations.

Apparatus

A CL-25 pen recording d.c. polarograph (ELICO, Hyderabad, India), an ELICO Model CL-10 pH meter and a Lingane-type H-cell were employed. The voltages were measured against a saturated calomel electrode. Pure Nitrogen gas is passed through the apparatus for about 15 minutes to remove dissolved oxygen.

RESULTS AND DISCUSSION

Typical polarogram of Iodate recorded in an acetate-acetic acid buffer solution of pH 5 is presented in Figure 1. The polarogram reveals the presence of two waves of 3:1 ratio under the experimental solutions. Studies on the effect of pH indicated that the polarographic wave has a well defined shape and large currents in solutions of pH 5. The studies on the height of the mercury column on the second wave

current indicated its kinetic nature since it remained constant with height of the mercury column from 40 to 80 Cm Table 1. The log plot studies on the kinetic current revealed the six electron reduction of the first wave and the two electron reduction of the second wave. Reduction currents of both the wavs varied linearly with the concentration of Iodate.

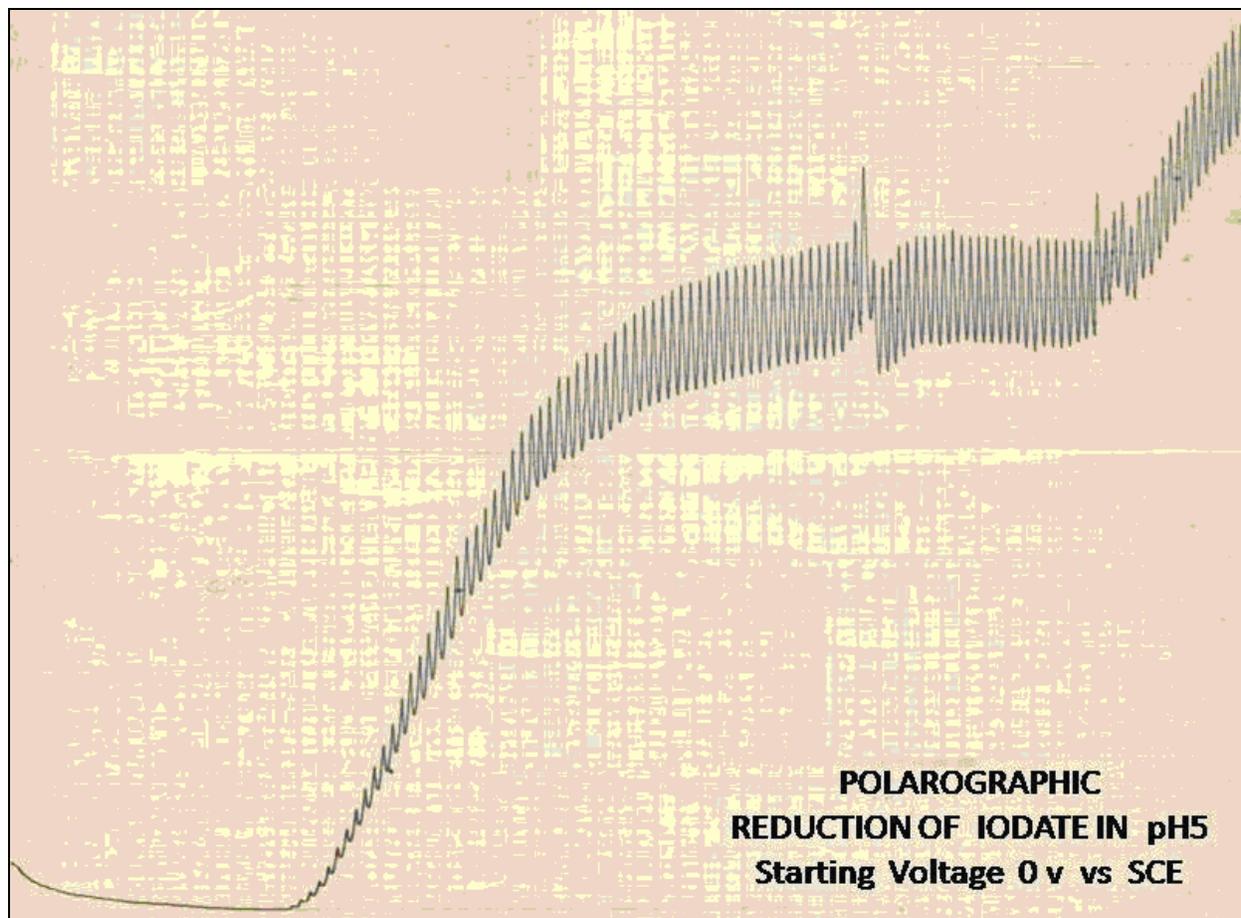
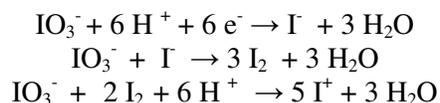


Fig.-1: Polarogram

Mechanism of the Electrode Process

The wave observed around -0.6 V against SCE pertains to the 6 electron reduction of Iodate to Iodide as reported by the earlier workers. The second wave observed around -1.62 V against SCE of two electron reduction has been attributed to the kinetic wave due to the formation of monovalent Iodine cation formed at the surface of the dropping mercury electrode due to the following chemical reactions.



Lang³ proposed that Iodate is responsible in presence of excess Iodide and hydrogen ions proceed through several stage leading to the formation of Iodine cation. Lang⁴ has developed methods in which the Iodine cation is stabilized by the formation of the Iodine- cyanide.



Further it is reported that electropositive monovalent Iodine is capable of combining with highly polarizable acid anions such as CN⁻, CNO⁻, CNS⁻ and so on. The pK_a values of Cyanic acid, Isocyanic acid and Thiocyanic acid are 9.21, 3.46 and 0.85 respectively. The pK_a value of acetic acid (4.76) is comparable with the former two acids. Therefore it is probable that acetate ion also combines with Iodine cation forming [I(CH₃COO)] analogous to [I(CN)], [I(CNO)] and [I(CNS)]. This ion is undergoing two electron reduction at the d.m.e yielding Iodide which is responsible for the appearance of the second wave at -1.62 V against SCE. Similar results are noticed in presence of cyanic, Isocyanic and Thiocyanic acid buffer solutions confirming the following mechanism.



The kinetic reduction of Iodate is dependant on its concentration since polarogram recorded at low concentration lack the two wave reduction of the Iodate reported. This confirms the kinetic nature of the wave and its surface nature. Since the concentration of Iodate as well as Iodide at the d.m.e are very low the kinetic reaction does not take place due to which neither the first wave of 6 electron reduction nor the second wave of 2 electron reduction are noticed.

Table-1: Effect of the mercury column height on the kinetic current
[IO₃⁻] = 1 X 10⁻³ M; pH = 5

Mercury column height (cms)	Kinetic current (μ A)	Half wave potential (- V vs SCE)
80	10	1.62
70	10	1.62
60	10	1.62
50	10	1.62
40	10	1.62

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