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CYCLIC VOLTAMMETRIC STUDIES ON IODINE AND IODIDE ION

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Cyclic voltammetric studies on I_2 and I^- were carried out on a platinum electrode in dimethylformamide. The studies included a variation in concentration and scan rate. The analysis of the data (i.e. i vs. $v^{1/2}$ and i vs. conc.) showed diffusion controlled reaction. The analysis of cyclic voltammetric data $(Ep)_c - (Ep)_a$ and $Ep - Ep/2$ rules out single step multielectron reductions. It is proposed that the reaction undergoes a series of ECE type reactions.

Key words: Cyclic voltammetric, Iodine, Electrochemical behaviour.

INTRODUCTION

Interests have been shown by various workers in the electrochemical behaviour of iodine and iodide/triodide ion [1-6]. Our interest in the electrochemical behaviour of iodine and iodide arose because of our studies on the charge transfer complex, 1-ethyl-4-carbomethoxy pyridinium iodide, (PyI) [7], and the reaction of Py. with methylviologen (MV^{2+}) to form a photoelectrochemical cell. PyI undergoes photochemical as well as electrochemical reaction as (eqns. 1,2).

$$\mathrm{PyI} \overset{h\nu}{\rightleftharpoons} \mathrm{Py.} + \mathrm{I.} \quad \dots\dots (1)$$

$$\mathrm{PyI} + e \rightarrow \mathrm{Py.} + \mathrm{I^-} \quad (2)$$

$$\mathrm{Py.} + \mathrm{MV^{2+}} \rightarrow \mathrm{MV.^{+}} + \mathrm{Py^{+}}$$

$$\mathrm{MV.^{+}} \rightleftharpoons \mathrm{MV^{2+}} + e.$$

We are interested in the subsequent reactions of eqns. (1) and (2)

$$\mathrm{Py.} + \mathrm{I.} \rightarrow \mathrm{PyI} \quad \dots\dots (3)$$

$$\mathrm{I.} + \mathrm{I.} \rightarrow \mathrm{I_2} \quad \dots\dots (4)$$

and

$$\mathrm{I.} + \mathrm{I^-} \rightleftharpoons \mathrm{I_2^-} \quad \dots\dots (5)$$

$$\mathrm{I_2} + \mathrm{I^-} \rightarrow \mathrm{I_3^-} \quad \dots\dots (6)$$

Electrochemically one may study the following reactions

$$\mathrm{I_2} + e \rightleftharpoons \mathrm{I_2^-} \quad \dots\dots (7)$$

$$\mathrm{I_2^-} \rightarrow \mathrm{I^-} + \mathrm{I.} \quad \dots\dots (8)$$

$$\mathrm{I^-} \rightarrow \mathrm{I.} + e \quad \dots\dots (9)$$

and

$$1. + 1. \rightarrow \mathrm{I_2} \quad \dots\dots (4)$$

etc.

depending upon the kinetics of electrochemical and chemical processes. Triangular wave cyclic voltammetry is a powerful analytical tool for studying electrochemical as well as chemical processes. If used judiciously information regarding details of homogeneous (preceding or following charge transfer) reactions and heterogenous rate constants can be obtained.

Thus triangular wave cyclic voltammetric studies on iodine and sodium iodide were carried out on a platinum electrode in dimethylformamide. Results of the studies are presented.

EXPERIMENTAL

The cyclic voltammetric studies were carried out using a PAR 174A Polarographic Analyzer. A Houston 0074 X-Y recorder was used to record the C.V. curves. The C.V's were recorded in a three electrode configuration with platinum disc as working electrode. All the electrode potentials are referred to a saturated calomel electrode (SCE). This SCE was seperated from the main compartment through a salt bridge. The platinum electrode was activated as usual [11]. The performance of the platinum electrode was checked with the cyclic voltammograms of *p*-anisylamine which is known to give completely reversible cyclic voltammogram [12].

Solvent dimethylformamide was either generally purified as described in the literature [10] or spectrograde solvents was used. All measurements were carried out at 25°.

RESULTS AND DISCUSSIONS

The complete cyclic voltammetric data of iodine and the iodide are presented in Table 1-3. The C.V. curves of iodine and iodide are presented in Figs. 1 and 2. The ip vs. $v^{1/2}$ (v = scan rate) and ip vs. concentration plots are given in Figs. 3-4.

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Generally iodine reductions are presented as [5-6].

$$3I_2 + 2e \rightarrow 2\,I_3^- \quad E_1 \ldots\ldots\ldots\ldots \quad (10)$$

$$2I_3^- + 4e \rightarrow 6\,I^- \quad E2 \ldots\ldots\ldots\ldots \quad (11)$$

only Vetter has proposed [8]

$$I + e \rightleftharpoons I^- \text{ or } 1/2\,I_2 + e \rightleftharpoons I^- \ldots\ldots \quad (12)$$

Eqns. [10] & [11] may be written as

$$I_2 + \frac{2}{3}\,e \rightleftharpoons \frac{2}{3}\,I_3^- \ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

$$I_3^- + 2\,e \rightleftharpoons 3\,I^- \ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

Where for 13 $n = \frac{2}{3}$ and for (14), $n = 2$.

For a reversible system without complication from chemical reaction, a cyclic voltammogram should exhibit

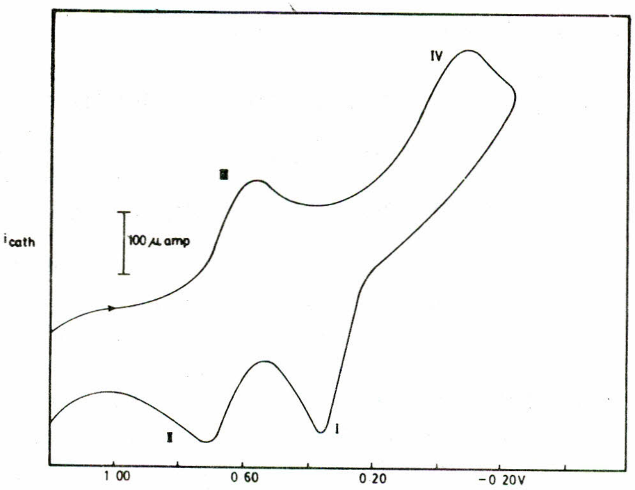

Fig. 1. Cyclic voltammogram of I_2 (2 mM), solvent dimethylformamide, scan rate 50 mv/sec, scan direction from + 1.20 V to 0.60 V vs. SCE.

Table 1. Cyclic voltammetric data of I_1 (From + 1.2 V to −0.4V)^{a,b}.

Conc. (mM)	Scan rate (mv/sec)	Wave	Anodic			Wave	Cathodic		
			ip^b	Ep	Ep/2		ip^b	Ep	Ep/2
4	200	I	800	0.400	0.30	IV	750	− 0.240	0.030
		II	550	0.785	0.70	III	750	0.50	0.660
	50	I	300	0.38	0.30	IV	380	− 0.20	0.000
		II	360	0.75	0.665	III	400	0.57	0.685
	10	I	160	0.32	0.24	IV	250	− 0.14	0.100
		II	185	0.72	0.64	III	190	0.600	0.690
3	200	I	580	0.420	0.335	IV	600	− 0.210	− 0.030
		II	420	0.790	0.690	III	560	0.510	0.470
	50	I	240	0.395	0.320	IV	270	− 0.220	− 0.030
		II	220	0.745	0.660	III	280	0.530	0.670
	10	I	85	0.370	0.300	IV	140	− 0.160	0.170
		II	105	0.730	0.650	III	110	0.600	0.700
2	200	I	500	0.390	0.300	IV	460	− 0.17	0.020
		II	300	0.740	0.650	III	400	0.54	0.675
	50	I	250	0.363	0.290	IV	240	− 0.095	0.080
		II	160	0.720	0.630	III	195	0.580	0.690
	10	I	85	0.370	0.300	IV	130	− 0.080	0.150
		II	76	0.720	0.630	III	85	0.605	0.700
1.	200	I	270	0.440	0.325	IV	190	− 0.170	− 0.050
		II	55	0.745	0.700	III	160	0.520	0.675
	50	I	185	0.380	0.285	IV	162	− 0.12	0.135
		II	20	0.675	0.630	III	60	0.50	0.70
	10	I	100	V. broad		IV	80	0.00	0.20
		II	5	0.66		III	30	0.57	0.70

(a) Solvent DMF, working electrode Platnium Disc; ref. electrode SCE; scan direction from + 1.20 V to −0.6 V; (b) in microampere.

$$E_p - E_{p/2} = \frac{58}{n}\ \text{mv}$$

$$(E_p)_c - (E_p)_a = \frac{60}{n}\ \text{mv}$$

which, for process [13], should come out to be 87 mv and 90 mv respectively, while for the process given by (14) both should be around 30 mv. From the data shown in Table 1-3 it is clear that these conditions are not followed.

It is thus obvious that neither reaction (13) nor (14) involves a single step. These two processes (13 and 14) depict overall reactions.

As regards to Vetter's proposed mechanism, one has to accept the existence of the species 1/2 (I_2) or I atom before electrolysis takes place!

To explain the overall processes given above, it is proposed that the following elementry steps are involved.

For

$$31_2 + 2e \rightleftharpoons 21_3^-$$

one has

$$1_2 + e \overset{k_h1}{\rightleftharpoons} I_2^-$$

$$I_2^- \overset{k_1}{\rightarrow} 1 + I^- \qquad (b)$$

$$1_2 + I^- \overset{k_2}{\rightarrow} I_3^- \qquad (c)$$

$$I_2 + I \overset{k_3}{\rightarrow} I_3 \qquad (d)$$

$$I_3 + e \overset{k_h2}{\rightleftharpoons} I_3^- \qquad (e)$$

$$31_2 + 2e = 21_3^- \qquad (f)$$

For

$$I^3 + 2e \rightleftharpoons 31^-$$

on has

$$1_3^- + e \overset{k_{h1}}{\rightleftharpoons} 1_3^{2-} \qquad 17(a)$$

$$1_3^{2-} \overset{k_1}{\rightarrow} I^- + I_2^- \qquad (b)$$

$$I'_2 + e \overset{k_{h2}}{\rightleftharpoons} I_2^{2-} \qquad (c)$$

$$I_2^{2-} \overset{k_2}{\rightarrow} 21^- \qquad (d)$$

$$I_3^- + 2e \rightleftharpoons 31^- \qquad (e)$$

where k_i and k_{hi} are the homogeneous and heterogeneous rate constants respectively.

Thus for iodine, scaning from + 1.2 to -0.6 (i.e. -ve direction) the first reduction peak (Marked III) corresponds

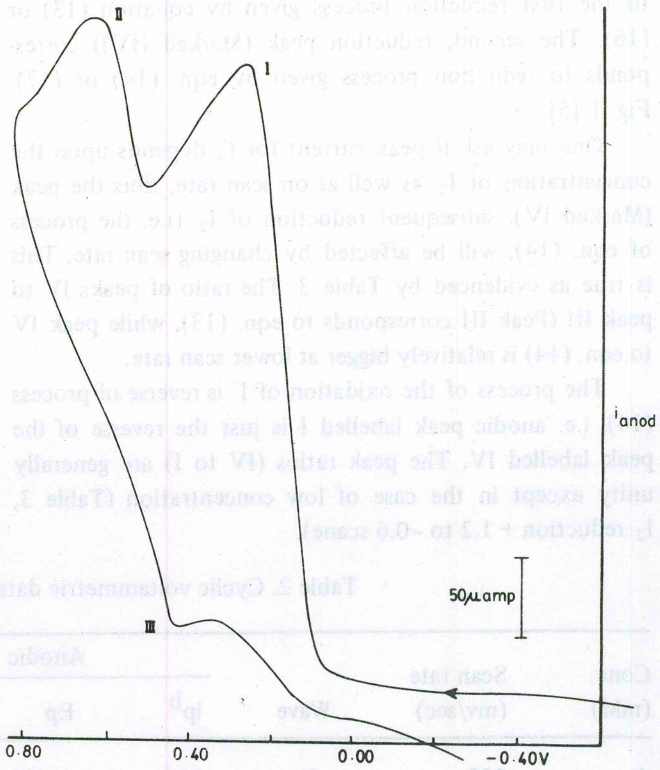

Fig. 2. Cyclic voltammogram of NaI (4 mM), solvent dimethylformamide; scan rate 50 mv/sec; scan direction -0.40 V to 1.20 V vs. SCE.

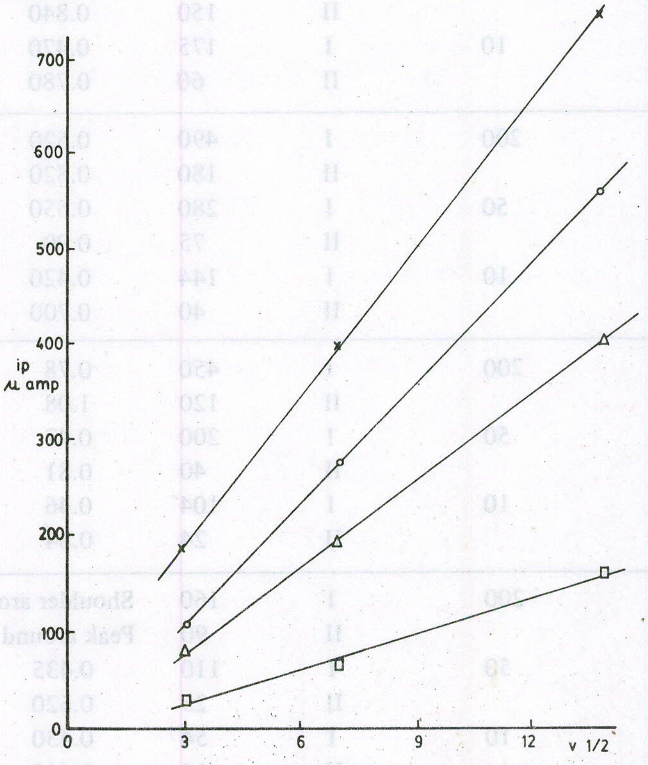

Fig. 3. ip vs. $v^{1/2}$; I_2; scan direction + 1.20 to -0.60 V (vs. SCE); wave III of Fig. 1. X = 4 mM, 0 = 3 mM, △ = 2 mM, □ = 1 mM concentration.

to the first reduction process given by equation (13) or (16). The second, reduction peak (Marked (IV)) corresponds to reduction process given by eqn. (14) or (17). Fig. 1 [5].

One may ask if peak current for I_3^- depends upon the concentration of I_2 as well as on scan rate, thus the peak (Marked IV), subsequent reduction of I_2 (i.e. the process of eqn. (14), will be affected by changing scan rate. This is true as evidenced by Table 3. The ratio of peaks IV to peak III (Peak III corresponds to eqn. (13), while peak IV to eqn. (14) is relatively bigger at lower scan rate.

The process of the oxidation of I^- is reverse of process (14), i.e. anodic peak labelled I is just the reverse of the peak labelled IV. The peak ratios (IV to I) are generally unity except in the case of low concentration (Table 3, I_2 reduction + 1.2 to -0.6 scane).

One may ask further whether reduction of I_2 (peak III) or I_3^- (IV) or oxidation (II, I, respectively), according to the above detailed mechanism, depends upon the concentration of I^-, except through the usual diffusion equation. Peak ratio III/I could give some information. The ratio is not affected by scan rate except for low concentration (Table III). At the same time the linearity of ip vs conc., and ip vs. $v^{1/2}$ curves, show that the processes as a whole are diffusion controlled [8(b)].

Looking at the cyclic voltammogram of NaI, it is apparent that it differs from that of I_2 in the respect that wave III is quite small while wave IV is like a shoulder. The reason for this behaviour is not apparent. The C.V pattern remains unchanged for scan rates ranging from 10 mv/s to 200 mv/s and concentration ranging from 1mM to 4mM. It is all the more intriguing that in propylene carbonate all

Table 2. Cyclic voltammetric data of NaI (From -0.60 V to 1.20 V)[a,b].

Conc. (mM)	Scan rate (mv/sec)	Anodic				Cathodic			
		Wave	ip[b]	Ep	Ep/2	Wave	ip	Ep	Ep/2
4	200	I	730	0.480	0.370	IV	–	Shoulder	–
		II	320	0.850	0.740	III	350	0.60	0.54
	50	I	375	0.470	0.370	IV	–	Shoulder	–
		II	150	0.840	0.760	III	125	0.630	0.730
	10	I	175	0.470	0.350	IV	–	Shoulder	–
		II	60	0.780	0.720	III	60	0.66	0.72
3	200	I	490	0.520	0.390	IV	160	– 0.160	0.000
		II	180	0.820	0.730	III	200	0.600	0.700
	50	I	280	0.550	0.380	–	c	Shoulder at	0.30
		II	75	0.90	0.660	–	c	c	–
	10	I	144	0.420	0.360	IV	c	c	0.06
		II	40	0.700	0.620	III	56	0.620	0.680
2	200	I	450	0.78	0.54	IV	c	–	–
		II	120	1.08	1.01	III	c	–	–
	50	I	200	0.47	0.36	IV	c	–	–
		II	40	0.81	0.75	III	c	Shoulder at 0.62	
	10	I	104	0.46	0.36	IV	c	–	–
		II	24	0.84	0.76	III	c	Inflection	
1	200	I	160	Shoulder around	0.46	–	c	–	–
		II	90	Peak around	0.70	–	–	–	–
	50	I	110	0.435	0.340	–	c	–	–
		II	25	0.620	0.550	–	c	–	–
	10	I	54	0.430	0.340	–	c	–	–
		II	16	0.615	0.530	–	c	–	–

(a) See foot note Table 1. Scaning from -0.60 V to + 1.20 V; (b) See foot notes Table 1; (c) Not measureable.

Table 3. Ratio of the peak currents[a].

Substrate and scan direction	Conc mM	Scan rate mv/sec	II/I	III/I	IV/III	IV/I
I_2; From + 1.20 to 0.60	4	200	0.69	1. 8	1.00	1.06
		50	1.20	1.11	0.95	0.71
		10	1.10	1.02	1.31	1.16
	3	200	0.72	1.04	1.07	1.42
		50	0.91	1.27	0.96	0.83
		10	1.23	1.33	1.27	0.78
	2	200	0.60	1. 3	1.15	1.44
		50	0.64	1.21	1.23	1.58
		10	0.89	1.10	1.52	1.55
	1	200	0.20	2.91	1.18	2.02
		50	0.11	3.00	2.70	8.18
		10	0.05	6.00	2.66	8.86
NaI, From – 0.60 to + 1.20	4	200	0.43	1.09	–b	–b
		50	0.40	0.83	–b	–b
		10	0.34	1.00	–b	–b
	3	200	0.37	1.11	0.80	–b
		50	0.27	–b	–b	–b
		10	0.27	1.40	–b	–b
	2	200	0.27	–b	–b	–b
		50	0.20	–b	–b	–b
		10	0.23	–b	–b	–b
	1	200	–b	–b	–b	–b
		50	0.23	–b	–b	–b
		10	0.30	–b	–b	–b

(a) I, II, III, IV means wave, I, II, III, IV and II/I etc. mean $(ip)_{II}/(ip)_{1\ etc.}$; (b) not measureable.

the waves (I to IV) are distinctly present [9]. This should be pursued further.

It was pointed out before that $E_p - E_{p/2}$ and $(E_p)_c - (E_p)_a$ both are much greater that 60 mv. This could mean that either the processes are quasireversible or multistep. Since ip vs $v^{1/2}$ and ip vs conc. curves are generally linear, hence quasireversible cases are ruled out. Also since there are no two consective electrode processes apparent with $E_{1/2}$ less than 100 mv, no disproportionation constant could be calculated. Also it is not a simple ECE mechanism.

In conclusion one may say that the reduction of iodine or the oxidation of I does not involve a single step one-, or two- or three- electron transfer and instead they undergo a series of complicated ECE type reactions, these may perhaps be studied by pulse radiolysis. The data shown in Table 1-3 suggests that neither of the reaction is quasireversible.

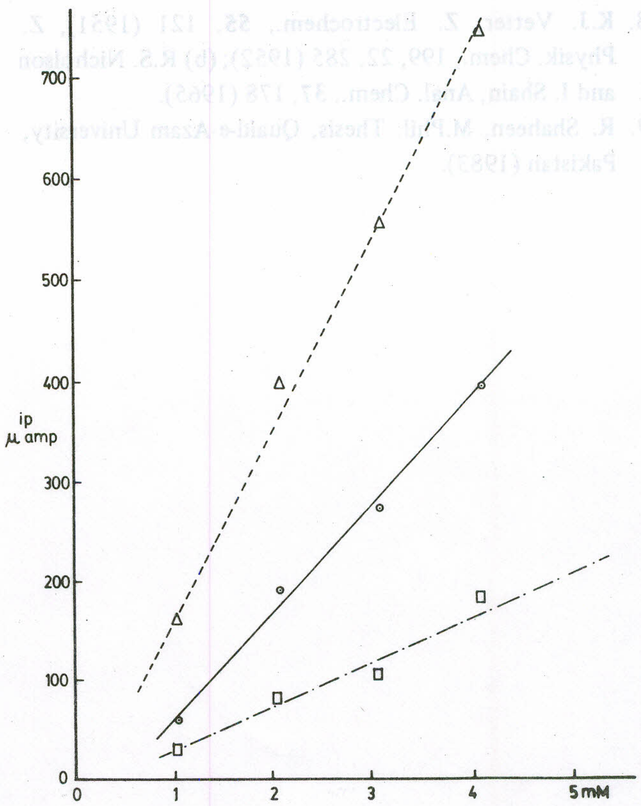

Fig. 4. ip vs. concentration; I_2, scan direction + 1.20 to – 0.60 V. (vs. SCE), wave III of Fig. 1. □ = 10 mM, 0 = 50mv △ = 200 mv per sec. scan rate.

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