Pulse Polarography of Iodate, Bromate and Periodate Ions

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The pulse polarography of iodate, bromate and periodate at a dme was studied in different buffer solutions. The Oldham and Parry methods of analysis were applied to the reduction waves and the kinetic parameters of the totally irreversible electroreduction were determined. A general mechanism for the reduction process of IO_3^-, BrO_3^- and IO_4^- was suggested. The applicability of the pulse technique for quantitative determination of the investigated oxyanions was also considered.

The polarographic behaviour of iodate, bromate and periodate ions by direct current technique at the DME was the subject of several investigations (1-12). It was found that the irreversible waves of these ions were dependent on the type and concentration of the supporting electrolyte. The morphology of the reduction wave of some oxyanions in presence of surfactants revealed the adsorption effect of electrochemically inactive surfactant at the charged interface(5-9). The present investigation is devoted to the study of pulse polarographic behaviour of IO_3^-, BrO_3^- and IO_4^- in solutions of varying pH in order to explore the potentialities of pulse polarography for the evalution of the kinetic parameters of totally irreversible electro reductions.

EXPERIMENTAL

Reagents

All chemicals used were of analytical grade. 0.01 M solutions of KIO_3, $KBrO_3$ and KIO_4 were prepared by dissolving the accurate weights of the solids in twice distilled deionized water and standardized by recommended methods (13). The modified universal buffer series of Britton and Robinson (pH 2-12) (14) was prepared. pH's were checked using a Radiometer pH meter Model 28, accuracy ±0.005 unit.

Instruments

Pulse polarograms were obtained with a Princeton Applied Research (PAR) Model 174A polarographic analyzer equipped with PAR Model 172A Drop Timer and Electrode Assembly. Polarograms were recorded on Hewlett-Packard X-Y recorder 7045A. A thermostated Metrohm cell with a three electrode system (DME, SCE and Pt wire electrodes) was used. The DME used had the following characteristics m=0.65 mg/sec , natural drop time t=5.5 sec at open circuit in 1 M KCl . All measurement were made at 25°C. The solution was deacrated by passing a slow stream of pure, presaturated nitrogen through the cell for 45 min. The pulse polarographic mode was used with a pulse duration of 57 ms, drop time 2 sec and a scan rate of 2 mV/sec, except where otherwise indicated.

The coulmetric method of De Vries and Kroon (15) using a mercury pool cathode was used for determining the value of n, the number of electrons involved in the reduction process.

RESULTS AND DISCUSSIONS

PULSE POLAROGRAPHY OF IODATE IONS

The polarograms representing the pulse polarographic behaviour of IO_3^- in universal buffer solutions are given in Fig.1. Pulse polarographic

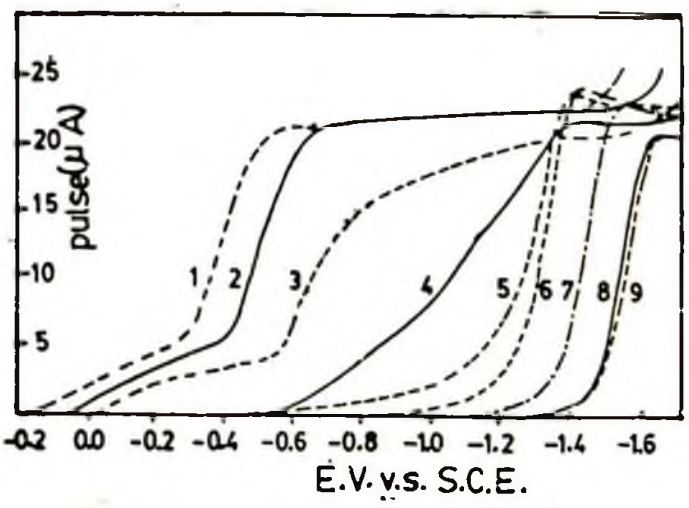


Fig. 1 Pulse polarograms of 6×10^{-4} M of iodate ions in universal buffer solutions.

pH of the Buffer:

1) 3.0, 2) 3.9, 3) 4.7, 4) 5.6, 5) 6.6
6) 7.4, 7) 8.3, 8) 9.3 and 9) 10.1 .

current/voltage curves of IO_3^- in acid solutions (pH 4.7) show a well defined wave corresponding to direct reduction of IO_3^- to I^-. As the pH of the medium increases, the reduction occurs along two waves. At pH's above 8, the first pulse wave appears to have decreased whereas the second reduction wave grows till reacting a constant value.

PULSE POLAROGRAPHY OF BROMATE IONS

The pulse polarograms of bromate ions in different buffer solutions show a well defined wave which corresponds to the direct reduction of bromate to bromide ions. (Fig.2). The height decreases with

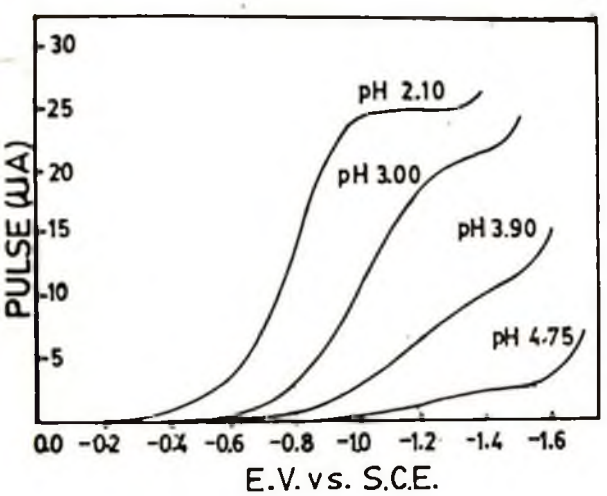


Fig. 2 Pulse polarograms of 2.5×10^{-4} M of bromate ions in universal buffer solutions.

pH= The limiting pulse current decrease with pH is analogous to an acid dissociation curve. It appears that the protonation kinetics contribute progressively to the reduction. The potential of the reduction pulse wave shifted to more negative values with increase of the pH value. Such behaviour indicates a change in the extent of protonation in the electrode process.

PULSE POLAROGRAPHY OF PERIODATE IONS

The pulse polarographic behaviour of periodate in universal buffer solutions of pH 3.0 - 10.1 is recorded and the curves obtained are shown in Fig.3. In acidic buffer solutions the polarographic reduction of IO_4^- occurs along two consecutive waves. The first wave is assigned to the reduction of IO_4^-/IO_3^- whereas the second wave represents the IO_3^-/I^- reduction. The limiting

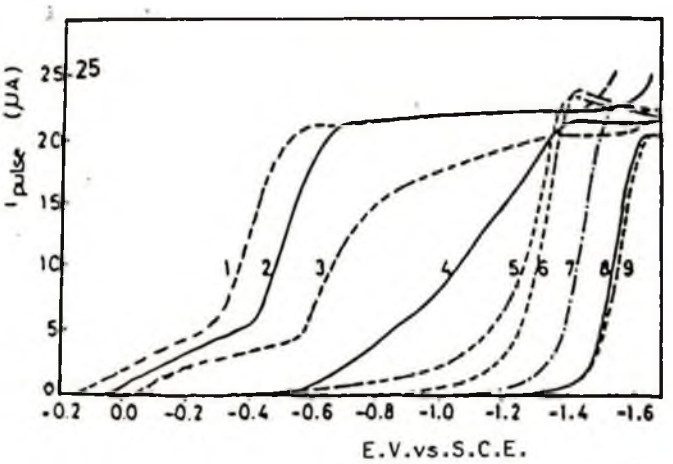


Fig. 3 Pulse polarograms of 2.5×10^{-4} M of periodate ions in universal buffer solutions. 1) pH 3.0, 2) 3.9, 3) 4.7, 4) 5.6, 5) 6.8, 6) 7.4, 7) 8.3, 8) 9.3 and 9) 10.1 .

pulse current of both waves increases proportionally to the concentration of periodate whilst the addition of increasing amounts of iodate produces a proportional growth of the second wave and the height of the first wave remains unchanged. The reduction of periodate to iodate involves two electrons and iodate to iodide involves six electrons (7,8). At pH above 7.4, the split waves combine together forming a single wave which occurs at more negative potential. The wave shifts to more negative potential with rise of pH whilst the pulse limiting current remains fairly constant.

KINETIC PARAMETERS OF THE ELECTRODE PROCESS

The kinetic parameters of electrode processes can be calculated from pulse polarograms according to the method proposed by Oldham and Parry (16) using the equation.

$$\frac{0.0592}{\alpha n_a} \log \left[\frac{X^2 \ (1.75 + X^2)}{(1 - X)} \right] = E_{1/2} - E_{de} \quad (1)$$

Where X is defined as the ratio of the current i (for time t and potential E) to the limiting current (for the same value of time t but at more negative potential). The plot of log. $[X^2(1.75+X^2)/(1-X)$ vs. $(-E)$ gives a straight line and the slope is equal $\alpha n_a/0.0592$ volt at 25°C. The intercept is equal to $E_{1/2}$ which yields the heterogeneous rate constant K_f at the potential E_r using the following equation:

$$E_{1/2} = E_r + \frac{0.0592}{\alpha n_a} \log \left[2.31 \ K_f \sqrt{\frac{t^*}{D}} \right] \quad (2)$$

Where t* is the time delay of the measuring interval within the voltage pulse and D is the diffusion coefficient of the depolariser. The determination of the rate constant k_f at some convenient potential E_f is perferable in the case of an irreversible electrode reaction as the standard potential is mostly unknown. The different kinetic parameters of IO_3^-, BrO_3^- and IO_4^- at different pH values are given in tables 1 and 2. The resulting values of the kinetic parameters

TABLE 1

KINETIC PARAMETERS OF IO_3^- REDUCTION AT DIFFERENT PH VALUES

pH	$E_{1/2}$ V.	k_f cm/sec	αn_a	n_a α=0.3	α=0.5	α=0.7
3.00	-0.395	3.45×10^{-6}	0.295	0.98	0.59	0.42
3.95	-0.490	1.80×10^{-7}	0.395	I.19	0.71	0.51
4.70	-0.595	2.08×10^{-8}	0.381	1.27	0.76	0.54
5.60[a]	-0.680	6.32×10^{-8}	0.315	1.05	0.63	0.45
5.60[b]	-1.145	2.25×10^{-9}	0.271	0.90	0.54	0.38
6.80	-1.260	6.60×10^{-13}	0.389	1.29	0.77	0.56
7.40	-1.305	1.10×10^{-17}	0.560	1.86	1.12	0.80
8.30	-1.320	1.47×10^{-20}	0.661	2.20	1.32	0.94
9.30	-1.325	3.40×10^{-21}	0.685	2.28	1.37	0.97

a) 1st wave, b) 2nd wave.

TABLE 2

KINETIC PARAMETERS OF BrO_3^- AND IO_4^- REDUCTIONS AT DIFFERENT pH VALUES

pH	$E_{1/2}$ V.	k_f cm/sec	αn_a	n_a α=0.3	α=0.5	α=0.7
2.10	-0.78[a]	7.88x10	0.221	0.737	0.442	0.316
3.00	-0.99[a]	2.65x10	0.206	0.687	0.414	0.294
3.90	-1.16[a]	1.82x10	0.188	0.626	0.376	0.268
3.00*	-0.36[b]	1.63x10	0.247	0.823	0.494	0.350
4.75*	-0.66[b]	4.17x10	0.269	0.869	0.538	0.384
6.80*	-0.74[b]	1.20x10	0.278	0.927	0.556	0.397
7.40	-1.34[b]	1.12x10	0.362	1.206	0.724	0.517
8.30	-1.43[b]	1.26x10	0.516	1.720	1.032	0.737
9.30	-1.51[b]	5.24x10	0.539	1.796	1.078	0.770

* 2nd wave a. Bromate b. Periodate

confirmed that the electrode reaction proceed irreversibly. This is substantiated by the fact that the value of α is less than unity even when the number of electrons in the rate determining step is taken equal to one electron. The pulse polarographic half wave potential, $E_{1/2}$, steadily shifts to negative value as the pH of solution increase. At the same time, the values of heterogeneous rate constant, k_f decreased. This indicates that the reduction process becomes more difficult and irreversible with increasing pH. The rate of electron transfer decreases due to a slower reaction probably due to decreased protonation.

REDUCTION MECHANISM

In order to throw light on the mode of reduction of IO_3^-, BrO_3^- and IO_4^-, it was necessary to calculate the number of electrons involved in the reduction by applying the coulmetric method of De Vries and Kroon (15). The coulmetric experiment applied at a potential on the plateau of the polarographic wave indicates a consumption of 6 electrons per molecule for the reduction of IO_3^- and BrO_3^- indicating the reduction is to I^- or Br^- state and 8 electrons per molecule in the overall reduction of IO_4^- where intial reduction to IO_3^- takes up 2 electrons.

The analysis of the reduction pulse waves by Oldham and Parry (16) method indicates that the reduction process is irreversible and is controlled by a single rate-determining step (tables 1 and 2). In this context it should be mentioned that the vacant level in iodic acid or bromic acid is lower than in iodate and bromate ions respectively(11) and consequently the reaction path for reduction mechanism for IO_3^- or BrO_3^- in acidic buffer solution represented by the following scheme.

$H^+ + XO_3^- = HXO_3$ (fast)
$HXO_3 + e = HXO_3^-$ (slow)
$HXO_3^- + 5H^+ + 5e = X^- + 3H_2O$ (fast)
($X^- = I^-$ or Br^-)

For basic media, where the number of electrons participating in the rate-determining step is double that in acid and neutral solutions and the reduction path for IO_3^- is assumed as follows :—

$M^+ + IO_3^- = MIO_3$ (fast)
$MIO_3 + 2e = IO_2^- + M^+ + O^{2-}$ (slow)
$O^{2-} + H_2O = 2OH^-$ (fast)
$IO_2^- + 2H_2O + 4e = I^- + 4OH^-$ (fast)

The dependence of the half-wave potential of periodate wave on pH leads to the conclusion that hydrogen ion is involved in the reduction process.

APPLICATION OF THE PULSE POLAROGRAPHIC TECHNIQUE FOR ANALYTICAL DETERMINATION OF IO_3^-, BrO_3^- AND IO_4^-

The applicability of the pulse technique as an analytical method for the determination of IO_3^-, BrO_3^- and IO_4^- was tested in various buffer solutions as a function of the depolarizer concentration. The limiting pulse current vs. concentration of the investigated oxyanions is linear. The detection limit is ca. 2.5×10^{-4} M.

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