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ELECTROCHEMICAL OXIDATION OF HYPOCHLORITE AT PLATINUM ANODES

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Abstract Oxidation of hypochlorite has been studied by cyclic voltammetry with a rotating-ring-disc assembly. Experiments were carried out with sodium chloride or sodium sulphate solutions with hypochlorite present or absent. Hypochlorite is oxidized at the platinum disc anode and the species formed by this oxidation are detected with the platinum ring cathode. From the shape of the current–potential curves at the ring electrode and from the relation between the ring and the disc currents it has been concluded that the first step of the hypochlorite oxidation is the formation of the chloroxyl radical (ClO).

INTRODUCTION

Chlorate can be formed by electrochemical oxidation of hypochlorite ions or hypochlorous acid molecules or by chemical reaction of these species. Several overall reactions have been given[1] for the electrochemical production of chlorate. Generally, the one given by Foerster[2] is accepted. However, the mechanism of the electrochemical formation of chlorate has not yet been elucidated. Only the first step of the oxidation of hypochlorite is examined in this investigation. The species formed during the oxidation of hypochlorite are detected by using a rotating-ring-disc assembly.

REACTIONS

Cyclic voltammetric experiments were carried out to elucidate the mechanism of hypochlorite oxidation. The oxidation and the reduction of hypochlorite are both interesting in explaining the results*. According to the literature[3], the reduction of hypochlorite ions and of hypochlorous acid molecules are respectively given by

$$ClO^- + H^+ + 2e^- \rightarrow Cl^- + OH^- \qquad (1a)$$

$$HClO + 2e^- \rightarrow Cl^- + OH^-, \qquad (1b)$$

and the oxidation of hypochlorite ions and hypochlorous acid molecules by

$$6ClO^- + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 6H^+ + 3/2O_2 + 6e^-, \qquad (2a)$$

$$6HClO^- + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 12H^+ + 3/2O_2 + 6e^-. \qquad (2b)$$

The ratio between the concentration of hypochlorite ions and hypochlorous acid molecules is determined by the equilibrium

$$HClO \rightleftharpoons ClO^- + H^+$$

where the equilibrium constant is 2.9×10^{-8} mol l^{-1}[4].

EXPERIMENTAL

The experiments were carried out in a classical three-compartment electrolysis cell with a rotating-ring-disc electrode assembly (RRDE) consisting of a platinum disc and a platinum ring which were embedded in Teflon. The characteristic data of the RRDE used are given in Table 1.

The compartment with the RRDE and that with the counter electrode, a smooth platinum sheet 5 cm^2 in area, were separated by a sintered glass disc. All potentials were measured *vs*, and referred to a saturated calomel electrode (*sce*). The potential of the disc or the ring was continuously changed at a constant scan rate between a maximum value, E_{max}, and a minimum value, E_{min}, by a voltage scan generator (Wenking, model VSG 72). The potential signal was given to a bipotentiostat (Tacussel, model BI-PAD). The ring current and/or the disc current were registrated by a recorder as a function of the ring and/or the disc potential(s). The temperature in the electrolytic cell was held constant at 298 K with a thermostat (Colora, model Ultra-Thermostat). NaClO solutions with an equivalent quantity of chloride were prepared by addition of chlorine gas to 1 M NaOH solutions and chloride-free NaClO-solutions by distillation of a 0.8 M technical NaClO solution to which $MgSO_4$ was added[5]. The stock solutions were kept at 273 K and used to obtain solutions about 0.02 M NaClO. A 1 M NaCl or 0.5 M Na_2SO_4 solution was used as the supporting electrolyte.

Before each series of experiments, the RRDE was

Table 1. Data of the RRDE

Collection factor	N_0	0.24
Shielding factor	S_0	0.60
Geometrical factor	β_0	0.48
Ring-surface area	A_R[cm^2]	0.146
Disc-surface area	A_D[cm^2]	0.502

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*The term hypochlorite is used to include both hypochlorite ions and undissociated hypochlorous acid.

cleaned by polishing with a 0.3 μm Al_2O_3 suspension, treating in an ultrasonic bath and by rinsing.

RESULTS AND DISCUSSION

Cyclic voltammograms for hypochlorite

In preliminary experiments reproducible voltammograms for oxidation as well as reduction of hypochlorite were obtained, when a potential range from -1.0 to about 2.0 V had been applied. When the potential was held at a fixed value, both the reduction and the oxidation current decreased at a decreasing rate as a function of time. Consequently, the RRDE experiments were generally performed at changing ring and constant disc potentials. This performance was necessary to quantitatively determine the products formed at the disc.

Figure 1 shows the i_R/E_R curves during the anodic and cathodic scans for a 1 M NaCl and 0.02 M NaClO solution with pH = 8.0 at a disc potential of 1.0 V, where i_D is practically zero. From this voltammogram it follows, that the direction of the potential scan clearly affects the i_R/E_R curve. The i_R/E_R curves for $E_D = 1.3$ V, where $i_D = 3.5$ mA, are given in Fig. 2. Comparing these with the curves of Fig. 1, it is concluded that an extra wave with a half-wave potential of 0.66 V occurs for a disc potential of 1.3 V. This means that a reducible species is produced on the disc at $E_D = 1.3$ V.

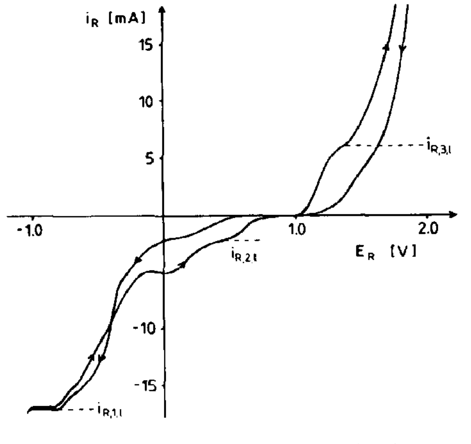

Fig. 1. The ring current, i_R, is plotted *vs* the ring potential, E_R, for a 0.02 M NaClO + 1 M NaCl solution at $E_D = 1.0$ V, pH = 8.0, $T = 298$ K and at a rotation speed of 64 rps and a scan rate of $v = 25$ mV s^{-1}.

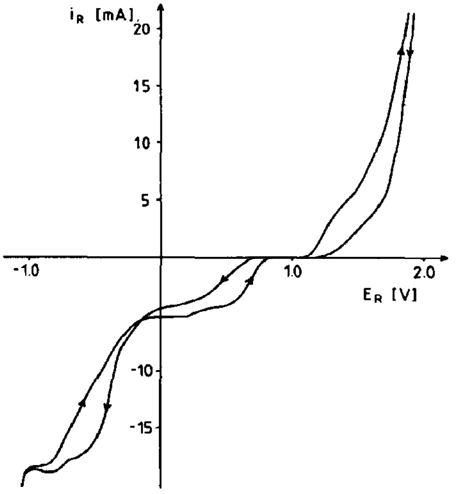

Fig. 2. The ring current, i_R, is plotted *vs* the ring potential, E_R, for a 0.02 M NaClO + 1 M NaCl solution at $E_D = 1.3$ V and the same conditions which are described under Fig. 1.

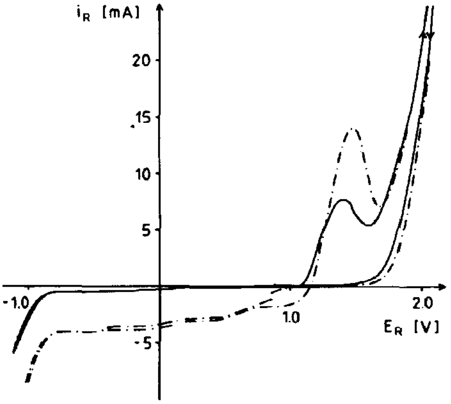

Fig. 3. The ring current, i_R, is lotted *vs* the ring potential, E_R, for a 1 M NaCl solution at a pH of 8.0, $T = 298$ K, $(\omega/2\pi) = 64$ rps and at $v = 25$ mV s^{-1}; solid line: $E_D = 1.3$ V; dotted line: $E_D = 1.9$ V.

Voltammograms of ClO_2^-, ClO_2 *and* ClO_3^-

The question arises as to which species, formed at the disc anode, are reduced at the ring. Figure 3 represents the voltammograms for a hypochlorite-free 1 M NaCl solution with a pH of 8.0 at $E_D = 1.9$ V where $i_D = 12$ mA. A reduction wave with $E_{1/2} = 1.11$ V clearly occurs for $E_D = 1.9$ V; it is likely that this is the reduction wave for molecular chlorine. The oxidation branch of the voltammograms in Fig. 3 are attributed to the oxidation of Cl^- to Cl_2[6]. During the anodic scan, a compound, for instance an oxide or a Cl–O species is formed on the platinum electrode surface. This compound slows down the rate of chloride oxidation[6]. Consequently, the maximum of the anodic peak does not depend on diffusion of chloride ions to the electrode surface.

In experiments with a hypochlorite-free 0.5 M Na_2SO_4 solution at pH = 8.0 the reduction of oxygen was observed at the ring with a half-wave potential of 0.16 V, when the disc was held at 1.9 V, where $i_D = 14$ mA. Thus, the oxygen-reduction wave does not interfere with the extra wave.

Voltammograms for a 0.5 M Na_2SO_4 + 0.02 M $NaClO_2$ solution are shown in Fig. 4. Chlorite is oxidized at lower potentials than hypochlorite and is not reduced at $E_R > 0.2$ V[7]. Reduction of chlordioxide is observed on the ring indicating formation of

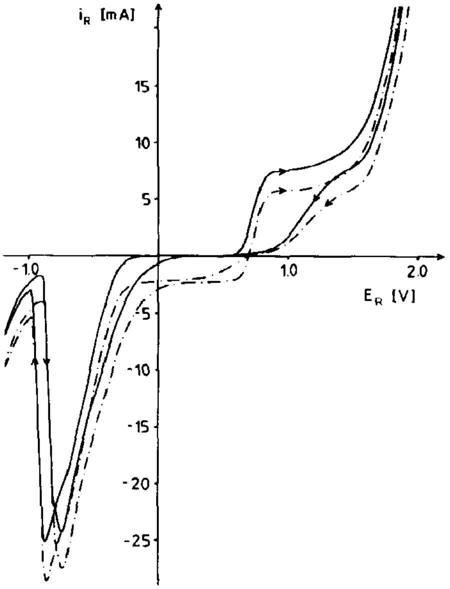

Fig. 4. The ring current, i_R, is plotted *vs* the ring potential for a 0.02 M $NaClO_2$ + 0.5 M Na_2SO_4 solution at a pH of 8.0, T = 298 K, $(\omega/2\pi)$ = 64 rps and at v = 250 mV s^{-1}; solid line: E_D = 0.5 V; dotted line: E_D = 1.3 V.

ClO_2 by oxidation of chlorite ions on the disc at E_D = 1.3 V (Fig. 4). The wave for the oxidation of ClO_2^- to ClO_2 has a half-wave potential of about 0.72 V *vs sce*. This value agrees with that found in the literature[8]. The slope of the i_R/E_R curve for the ClO_2 reduction is much higher than that for the reduction wave with $E_{1/2}$ = 0.66 V and shown in Fig. 2. Consequently, the extra wave with $E_{1/2}$ = 0.66 V in Fig. 2 is not caused by reduction of ClO_2. It also has been found that chlorate is not reduced at $E_D >$ − 1.0 V. From this result and from Figs 2–4 it follows that the extra wave in Fig. 2 cannot be attributed to Cl^-, ClO_2^-, ClO_2 or ClO_3^-. It must be concluded that the extra wave is caused by the reduction of another oxidation product of hypochlorite, whereby the chloroxyl radical is the most acceptable species.

Reduction of hypochlorite

The current–potential curve for the reduction of hypochlorite is very complex. From Fig. 1 it follows, that the maximum rate of the hypochlorite reduction occurs in the potential range from − 1.0 to − 0.8 V. The limiting current for the reduction of hypochlorite in this potential range is indicated by $i_{R,l,l}$ for the ring and $i_{D,l,l}$ for the disc electrode. In Fig. 5, $i_{R,l,l}$ is given as a function of the square root of the rotation rate for a 0.5 M Na_2SO_4 + 0.02 M NaClO solution with a pH = 8.0 and at a scan rate of 25 mV s^{-1}. This figure shows, that $i_{R,l,l}$ is a diffusion-limited current for the reduction of hypochlorite. Further, it has been found that the slope of the $i_{R,l,l}/(\omega/2\pi)^{1/2}$ does not depend on the pH for the pH range from 5 to 11.

The current at E = − 0.9 V during the anodic scan is equal or lower than $i_{R,l,l}$. The occurrence of hysteresis depends on the pH, the scan rate and the minimum reversal potential. The effect of the scan rate is illustrated in Fig. 6. Much hysteresis is obtained in the voltammogram at pH = 6.5 and a scan rate of 25 mV s^{-1}. However, practically no hysteresis occurs at a high sweep rate, *viz* 250 mV s^{-1}. It has been found that the current for the reduction of hypochlorite decreases continuously, when the potential is held constant at a value between − 0.8 and − 1.0 V. The disc current at E_R = − 0.9 V *vs* the disc potential for subsequent scans is given in Fig. 7. The i_D/E_D curves changed only slightly by this procedure, therefore only

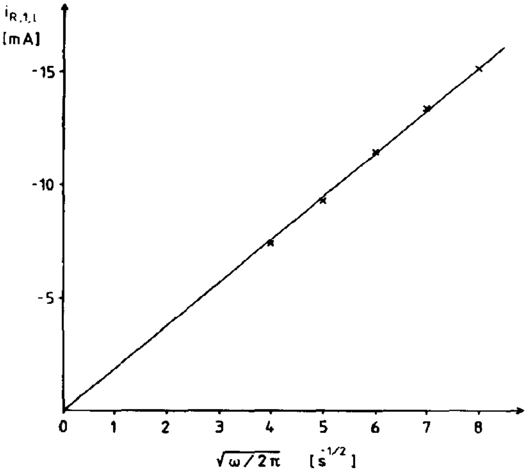

Fig. 5. The ring current of a hypochlorite reduction wave, $i_{R,l,l}$, is plotted *vs* $(\omega/2\pi)^{1/2}$ for a 0.02 M NaClO + 0.5 M Na_2SO_4 solution at pH = 8.0, T = 298 K, v = 25 mV s^{-1} and at E_D = 0.8 V.

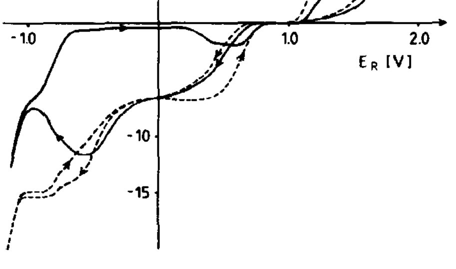

Fig. 6. Influence of the sweep rate on the hysteresis of ring current–ring potential curves for a platinum electrode in a 0.02 M NaClO + 1 M NaCl solution at pH = 6.5, T = 298 K and E_D = 0.8 V; solid line: v = 25 mV s^{-1}, dotted line: v = 250 mV s^{-1}.

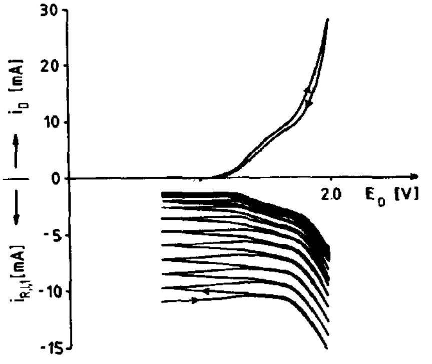

Fig. 7. The ring and disc currents are plotted *vs* the disc potential, E_D, for a 0.02 M NaClO and 1 M NaCl solution at pH = 8.0, $T = 298$ K, $(\omega/2\pi) = 64$ rps and $v = 100\ \mathrm{mV\,s^{-1}}$ and when the ring potential is kep at -0.9 V.

one i_D/E_D curve is shown. According to Fig. 7 i_R decreases with time until a quasi-steady state is reached and i_R increases with increasing i_D. The diffusivity for hypochlorite, (HClO + ClO$^-$), can be calculated with the Levich equation for the ring electrode giving

$$D_{\mathrm{hyp}}^{2/3} = \frac{i_{R,1,1}\cdot \nu^{1/6}}{0.62\, n\, F\, A_D \beta_0^{2/3} \omega^{1/2} c_{\mathrm{hyp}}}$$

where

n	is the number of electrons used for the reduction of hypochlorite
F	the Faraday constant
A_D	the disc electrode surface (cm^2)
β_0	the geometric factor
ω	the rotation rate (s^{-1})
ν	the kinematic viscosity (cm^2 s^{-1})
c_{hyp}	the total concentration of hypochlorite (mol cm^{-3})
$i_{R,1,1}$	the limited current of hypochlorite (A) and
D_{hyp}	the diffusion constant of hypochlorite (cm^2 s^{-1})

Introducing $F = 96500\ \mathrm{C\,mol^{-1}}$ electrons, $\nu = 1.23 \times 10^{-2}\ \mathrm{cm^2\,s^{-1}}$ [9], $n = 2$, $c_{\mathrm{hyp}} = 2.10^{-5}\ \mathrm{mol\,cm^{-3}}$, $\beta_0 = 0.48$ and $A_D = 0.502\ \mathrm{cm^2}$ into the Levich equation, it has been calculated from the slope of the $i_{R,1,1}/(\omega/2\pi)^{1/2}$ straight line (Fig. 5) that $D_{\mathrm{hyp}} = 1.10 \times 10^{-5}\ \mathrm{cm^2\,s^{-1}}$. This value lies in the range of diffusivities, *viz* from $0.82 \times 10^{-5}\ \mathrm{cm^2\,s^{-1}}$ to $1.30 \times 10^{-5}\ \mathrm{cm^2\,s^{-1}}$, reported by others[10, 11]. The difference between the diffusivities of ClO$^-$ and HClO is very slight and is neglected. Consequently, the limiting current $i_{R,1,1}$ is contributed to the reduction of hypochlorite to chloride. This agrees with the results of others, found under different experimental conditions[12, 13]. Since the main aim of this study is to investigate the oxidation of hypochlorite, the reduction branch is not discussed in detail. The reduction curve during the cathodic scan is rather straggling. An explanation is given by Schwarzer[10] and Mueller[13].

Oxidation of hypochlorite

Figure 1 shows a great hysteresis effect on the oxidation of hypochlorite. The oxidation wave is more clearly distinguished for the anodic scan than for the cathodic one. So that only the results for the anodic scan are discussed in detail. For i_D is practically zero and the conditions mentioned at Fig. 1, the limiting current for the oxidation during the anodic scan, $i_{R,3,1}$, is about 0.35 $i_{R,1,1}$ (Fig. 1). Since $i_{R,1,1}$ corresponds to $n = 2$, it follows that n would be 0.70 for the oxidation of one molecule of hypochlorite. It has been found that $i_{R,3,1}$ depends on the nature of the electrode, the scan range and the reversal potential. Similar results have been obtained for the disc electrode. The hysteresis effect becomes less with increasing minimum scan potential, E_{min}, and is practically repressed for $E_{\mathrm{min}} > 0.7$ V. A characteristic i_D/E_D curve is given in Fig. 7. Figure 8 shows $i_{D,3,1}$ as a function of $(\omega/2\pi)^{1/2}$ for a 0.02 M NaClO + 0.5 M Na$_2$SO$_4$ solution with a pH of 8.0 and at a scan rate of 100 mV s^{-1} in a potential range from 0.7 to 2.0 V. From this figure it follows that $i_{D,3,1}$ is proportional to $\omega^{1/2}$. The diffusion-limited current for the disc electrode can be calculated using the Levich equation, where $\beta_0 = 1$. The number of electrons used for the oxidation of one molecule of hypochlorite is unknown. From the slope of the $i_{D,3,1}/(\omega/2\pi)^{1/2}$ curve and with $D_{\mathrm{hyp}} = 1.10 \times 10^{-5}$ cm^2/s, it can be calculated that n would be 0.71. Though the potential scan ranges for the experiments of Figs 1 and 8 are quite different, *viz* -1.0 to 2.0 V and 0.7 to 2.0 V respectively, the calculated values for n are practically equal. Therefore it is very unlikely that poisoning of the electrode surface during the anodic sweep causes the low value of n. According to[14–17] hypochlorite ions are oxidized at potentials lower than 1.4 V and hypochlorous acid molecules are electrochemically inactive in this potential range.

Taking into account that the pH in the diffusion layer is not affected by this reaction and the dissociation constant for hypocclorous acid is $2.9 \times 10^{-8}\ \mathrm{mol\,l^{-1}}$[4], it follows that the ratio of ClO$^-$ to HClO is 74:26 at pH = 8.0. Taking this ratio into account, it follows that the number of electrons for the oxidation of one hypochlorite ion is $n = 0.96$. Consequently, chloroxyl radicals are formed by the oxdiation of exclusively hypochlorite ions.

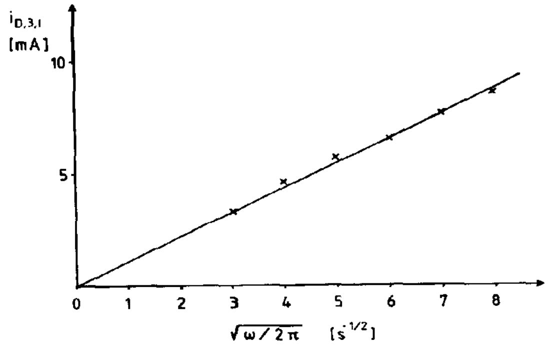

Fig. 8. The disc current of a hypochlorite oxidation wave, $i_{D,3,1}$, is plotted *vs* $(\omega/2\pi)^{1/2}$ for a platinum disc in a 0.02 M NaClO + 0.5 M Na$_2$SO$_4$ solution at pH = 8.0, $T = 298$ K, $v = 100\ \mathrm{mV\,s^{-1}}$ and at $E_D = 0.8$ V.

Reduction of the species formed by oxidation of hypochlorite

The hypochlorite reduction current and the oxidation current decrease with increasing time, holding the potential at a fixed value. Therefore experiments have been carried out at a constant ring and a changing disc potential. Fig. 7 shows $i_{R,1,l}$ at $E_R = -0.9$ V as a function of E_D for scans at various times.

From Fig. 7 it follows that, in a stationary state, $i_{R,1,l}$ increases continuously with increasing i_D in the i_D range as well, where only hypochlorite ions are oxidized. This means that hypochlorite is oxidized to a "higher" chlorine–oxygen compound, which is then transported to the ring electrode, where it is reduced to Cl^- at $E_R = -0.9$ V. Figs 1 and 2 also show an increasing ring current with an increasing disc current. This behaviour can be explained as follows: At the disc, hypochlorite ions are oxidized to chloroxyl radical, and the latter is reduced to ClO^- on the ring, resulting in the extra wave with a half-wave potential of 0.66 V. The limiting current for the reduction of the chloroxyl radical and that for HClO occur in the same potential range. Since only hypochlorite ions are oxidized at the disc anode, the pH at the disc electrode remains constant. This means that the concentration of hypochlorous acid is independent of the oxidation current of the disc, when only ClO^- ions are oxidized to ClO radicals. Thus the limiting current for the reduction of HClO at $E_R = 0.5$ V is independent of the disc current, *viz* $i^0_{R,2,l}$ is constant. Assuming further that a chloroxyl radical is reduced to ClO^- at $E_R = 0.5$ V, then

$$|i_{R,4,l}| = N_0 |i_D|,$$

where $i_{R,4,l}$ is the additional ring current at $E_R = 0.5$ V.

Table 2. Calculation of the limiting ring current of the extra reduction wave *vs* the disc current for a 0.02 M NaClO + 1 M NaCl solution with different pH. Parameters: see Fig. 9.

Solution pH	E_D [V]	$\lvert i_{R,2,l}\rvert$ [mA]	i_D [mA]	$\lvert i_{R,2,l}\rvert - \lvert i^0_{R,2,l}\rvert$ [mA]	$(\lvert i_{R,2,l}\rvert - \lvert i^0_{R,2,l}\rvert)/\lvert i_D\rvert$
8.0	1.0	1.35	0.0	0.0	0
	1.1	1.50	0.7	0.15	0.215
	1.2	2.15	3.9	0.80	0.205
	1.3	2.35	3.6	1.00	0.277
	1.4	2.50	4.8	1.15	0.240
	1.5	2.95	6.7	1.60	0.239
	1.6	3.45	8.2	2.10	0.256
	1.7	3.65	9.85	2.30	0.234
	1.8	3.85	9.8	2.50	0.255
9.5	0.8	0.30	0.0	0.0	0
	1.0	0.40	0.3	0.1	0.333
	1.2	0.80	2.3	0.5	0.217
	1.4	1.70	5.4	1.4	0.259
	1.6	2.60	9.6	2.3	0.240
	1.8	3.20	11.1	2.9	0.261
	2.0	4.30	18.6	4.0	0.215

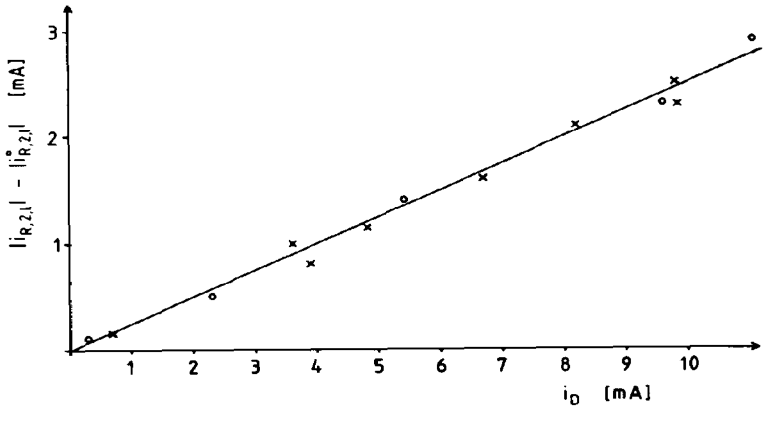

Fig. 9. The limiting ring current of the extra reduction wave, $|i_{R,2,l}|-|i^0_{R,2,l}|$, is plotted *vs* the disc current, i_D, for a 0.02 M NaClO + 1 M NaCl solution, whereby the disc potential is held at fixed values and the ring potential is scanned between −1.0 and 2.0 V. $T = 298$ K, $(\omega/2\pi) = 64$ rps; (×): pH = 8.0 and $v = 250$ mV s^{-1}; (o): pH = 9.5 and $v = 25$ mV s^{-1}.

The total limiting current for the ring at $E_R = 0.5$ V

$$|i_{R,2,l}| = |i^0_{R,2,l}| + N_0|i_D|.$$

From this relation it follows that

$$\frac{|i_{R,2,l}| - |i^0_{R,2,l}|}{|i_D|} = N_0$$

In Table 2, $(|i_{R,2,l}| - |i^0_{R,2,l}|)$ is given during the anodic sweep at various disc currents. In Fig. 9 the graphical representation of these data is given. From the slope of the straight line a collection factor of 0.25 is calculated, which is practically equal to the collection factor of N_0. From this result it may be concluded that hypochlorite ions can be oxidized to ClO radicals on the platinum disc and that chloroxyl radicals can be reduced to hypochlorite ions on the platinum ring at $E_R = 0.5$ V.

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