584. *Reactions of Hypochlorous Acid and Sodium Hypochlorite at the Dropping Mercury Electrode.*

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A set of double polarographic waves have been obtained, by use of the dropping mercury electrode, for 10^{-4}M-hypochlorous acid on step-wise neutralisation with sodium hydroxide. The waves are shown to represent the products of simple chemical reactions at the mercury surface.

AN earlier study of the polarography of hypochlorites in which the dropping mercury electrode was used (Heller and E. N. Jenkins, *Nature*, 1946, **158**, 706) was mainly concerned with the analysis of commercial sodium hypochlorite solutions, containing sodium chloride and dissolved oxygen, in the presence of chloramines. It was concluded that the hypochlorite ion is " one of the oxygen-containing anions which are irreversibly reducible at the dropping mercury electrode " with a half-wave potential $+0.08$ v. (saturated calomel electrode) in neutral 0·5N-potassium sulphate at room temperature. Further investigations by Heller and I. L. Jenkins (Jenkins, Thesis, Univ. of Wales, 1950) showed that acidified solutions of fairly chloride-free sodium hypochlorite gave double polarographic waves; these investigations were curtailed by the death of Dr. K. Heller while the results were yet inconclusive. The present work was aimed at obtaining reproducible polarograms of pure hypochlorous acid and sodium hypochlorite, at concentrations around 10^{-4}M. (where the curves are free from maxima) and in the presence of 0·1M-potassium nitrate, in order to establish the nature of the electrode processes.

EXPERIMENTAL.

Reagents.—Solutions of hypochlorous acid (about 0·1M.) were prepared in Pyrex apparatus, under the minimum of illumination, by chlorination of a suspension of yellow mercuric oxide, followed by distillation under water-pump vacuum. Chemical analysis of the solutions revealed no significant amounts of mercury salts, hydrochloric acid, or chlorous acid; the remaining oxy-acids of chlorine and their salts are not reducible at the dropping mercury electrode (Rylich, *Coll. Czech. Chem. Comm.*, 1935, **7**, 288). The solutions were relatively stable at room temperature if protected from light, losing as little as 1·5% of their initial strength in 4 weeks.

The potassium nitrate was a recrystallised analytical-grade specimen. All solutions were made up in conductivity water, prepared by the mixed-bed de-ionisation method (Davies and Nancollas, *Chem. and Ind.*, 1950, **7**, 129). The sodium hydroxide solution was carbonate-free.

Apparatus.—The manual polaroscope used consisted of a calibrated potentiometer wire, sensitive damped galvanometer, and Ayrton shunt. The Pyrex electrolysis cell, maintained at 25·0°, was fitted with a detachable, non-polarisable mercury–mercurous sulphate–saturated potassium sulphate half-cell of potential $+0.390 \pm 0.002$ v (against a saturated calomel electrode at 25°, with an intermediate solution of 0·1M-potassium nitrate. All potentials quoted hereafter are referred to the saturated calomel electrode). Electrical contact with the solution in the main cell was made around the periphery of an ungreased tap. The resistance thus introduced, about 20,000 ohms, was measured frequently and the potentials corrected for the IR drop across the cell. The dropping mercury electrode had the characteristics : $m = 1.68$ mg. sec.$^{-1}$ (fixed head of mercury); $t = 4.2$ sec. (-0.5 v, 0·1M-potassium nitrate).

Method.—Solutions were made up by weight, stock hypochlorous acid being added to the cell from a weight burette, with mechanical stirring and exclusion of oxygen. Mercury was not allowed to accumulate in the cell before start of the electrolysis, and the experiments were made under the

minimum of illumination. The mean values of the galvanometer oscillations were recorded. The bulk concentration of hypochlorite was reduced only very slowly by the mercury, as was demonstrated by amperometric and chemical analyses. The polarograms were corrected for the residual currents, previously determined.

RESULTS AND DISCUSSION.

The cathodic double wave obtained for 10^{-4}M-hypochlorous acid in $0 \cdot 1$M-potassium nitrate of pH 5·5 (Fig. 1, curve B) was perfectly reproducible. The results lose significance at potentials more positive than about $+0 \cdot 35$ v, owing to interference from the anodic dissolution wave of mercury. The overall limiting current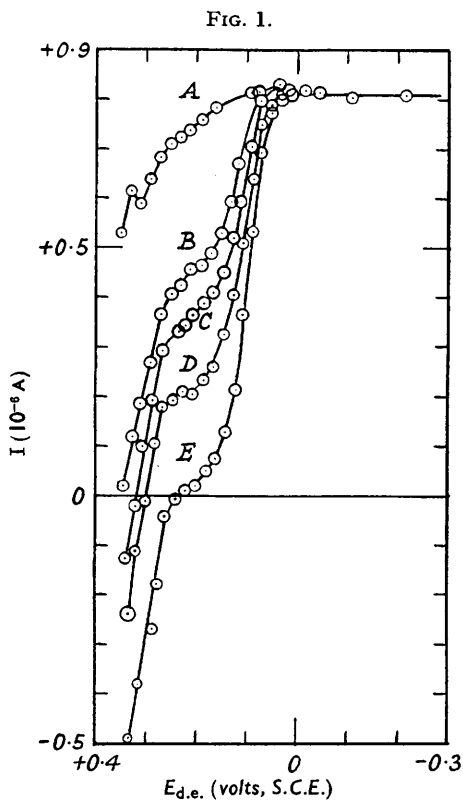s were measured at $-0 \cdot 50$ v, in solutions of strengths $2 \cdot 5 \times 10^{-5}$ to $3 \cdot 7 \times 10^{-4}$M., with and without added sodium hydroxide. In each " run," four or five successive additions of stock hypochlorous acid were made to the cell solution. While the ratio I_d/C remained constant within $\pm 2\%$ or better in a given " run," variations of up to 10% appear between the mean values of different " runs." These variations could not be correlated with the amount of added alkali, and may be caused by variations in the low " chlorine demand " of the freshly prepared supporting electrolyte solutions. Within the above limits, the ratio I_d/C is the same for undissociated hypochlorous acid as for the hypochlorite ion : their respective diffusion coefficients must then agree to within 20%. The specific conductivity of 1×10^{-3}M-sodium hypochlorite at 25° is $1 \cdot 15 \times 10^{-4}$ reciprocal ohms (Noyes and Wilson, *J. Amer. Chem. Soc.*, 1922, **44**, 1630), thus the equivalent ionic conductance of the hypochlorite ion is about 65 (on the assumption that $\Lambda_{Na}^{25} = 50$). By use of the equation $D = 2 \cdot 67 \times 10^{-7} \Lambda$, the diffusion coefficient of the hypochlorite ion may be calculated approximately as $1 \cdot 7 \times 10^{-5}$ cm.² sec.$^{-1}$. The highest mean value of I_d/C for hypochlorite solutions containing excess of alkali was $8 \cdot 5$ μA 1. millimol.$^{-1}$. Application of the Ilkovic equation, $n = I_d/605Cm^{\frac{2}{3}}t^{\frac{1}{6}}D^{\frac{1}{2}}$, yields $n = 1 \cdot 9$. If the correct value is assumed to be 2 electrons consumed per electrode process involving one hypochlorite ion, the diffusion coefficient may be recalculated as $1 \cdot 5 \times 10^{-5}$ cm.² sec.$^{-1}$ ($0 \cdot 5$M-potassium nitrate, 25°).

FIG. 1.

$E_{d.e.}$ (volts, S.C.E.)

The polarograms obtained for a series of approx. 10^{-4}M-hypochlorous acid solutions containing added acid or alkali (Fig. 1; Table) are free from maxima. The values of the electrolysis currents have been adjusted by an appropriate factor, where necessary, to bring the diffusion currents at $0 \cdot 0$ v. in each case to $0 \cdot 81$ μA (the mean value of I_d/C for this series being $8 \cdot 1$). The recorded pH values (glass electrode) are only approximate.

Half-wave potentials and currents for hypochlorite double waves.

$\dfrac{[\text{NaOH}]}{[\text{HOCl}]}$ or $\dfrac{[\text{HNO}_3]}{[\text{HOCl}]}$	pH	Curve	$E'_{\frac{1}{2}}$ (v)	$E''_{\frac{1}{2}}$ (v)	I' (μA)	I'' (μA)
1·07 (HNO₃)	4·4	A	—	—	—	—
0·00	5·5	B	+0·298	+0·122	0·46	0·35
0·20 (NaOH)	6·2	C	+0·303	+0·109	0·545	0·44
0·365 ,,	6·7	—	+0·288	+0·084	0·36	0·54
0·60 ,,	7·5	D	+0·308	+0·107	0·525	0·605
0·775 ,,	9·0	—	+0·294	+0·102	0·57	0·675
1·00 ,,	9·8	E	+0·297	+0·099	0·58	0·79

In the Table, $E'_{\frac{1}{2}}$ and I' are the half-wave potential and height respectively of the initial cathodic, anodic, or composite anodic-cathodic wave ($+0 \cdot 35$ to $+0 \cdot 20$ v); $E''_{\frac{1}{2}}$ and I'' refer to the subsequent cathodic wave. From Fig. 2, the ratio I''/I_d is seen to increase linearly with the

ratio $[NaOH]_{added}/[HOCl]_{added}$, rather than with any of the equilibrium ratios $[OCl^-]/([OCl^-] + [HOCl])$, calculated for a dissociation constant, K_{HOCl}, in the range 10^{-7}—10^{-8}. (Various values for K_{HOCl} appear in the literature; recent determinations at 25° are largely within the above range.) Curves *B*—*E* of Fig. 1 form a series of double waves of approximately constant half-wave potentials ($+0.30$ and $+0.10$ v respectively). Whereas the magnitude of the first wave remains roughly constant, the second wave increases linearly with the amount of added alkali, from about half the overall cathodic limiting current (hypochlorous acid) to almost the entire limiting current (sodium hypochlorite). These results may be interpreted in terms of an immediate chemical reaction of hypochlorous acid and sodium hypochlorite respectively at the mercury surface (Wolters, *J. pr. Chem.*, 1873, **7**, 468; 1874, **10**, 128) :

(i) $2HOCl + 2Hg = (HgO + HgCl_2) + H_2O.$
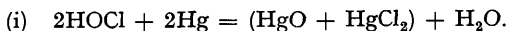
Under the conditions of the present experiments, the compounds in parentheses do not appear to exist as an oxychloride Hg_2OCl_2, and the mercuric chloride is immediately and almost

FIG. 2.

FIG. 3.

$----$ $[OCl^-]/([OCl^-] + [HOCl])$.
$\bigcirc$ $[NaOH]_{added}/[HOCl]_{added}$.
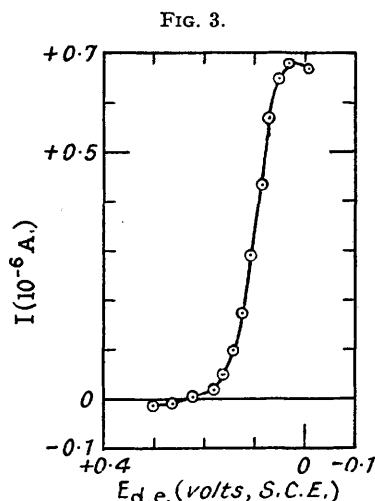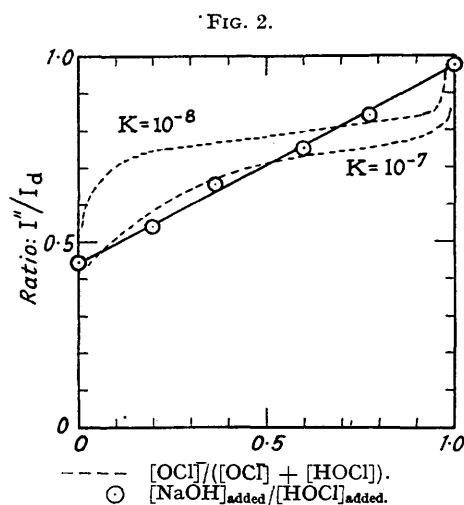
completely converted into calomel (Kolthoff and Miller, *J. Amer. Chem. Soc.*, 1941, **63**, 2732) :

(ii) $NaOCl$ (or $NaOH + HOCl$ in hydrolysis equilibrium) $+ Hg = HgO + NaCl (+H_2O)$.
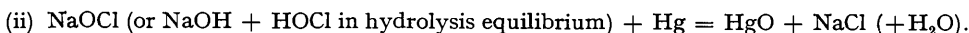
The first of the hypochlorite double waves is then caused by the reversible cathodic reduction of calomel, the reversible anodic depolarisation of mercury by chloride ion, or by mixed anodic-cathodic processes. Since the total chloride content as (chloride ion plus combined chlorine in calomel) remains constant throughout the series, the height, half-wave potential, and equation of the wave do not change. Kolthoff and Miller report a value of $+0.25$ v, both for the half-wave potential of 10^{-3}M-chloride (*J. Amer. Chem. Soc.*, 1941, **63**, 1405) and for the half-wave potential of 0.5×10^{-3}M-mercuric chloride (*ibid.*, p. 2732). A ten-fold decrease in these concentrations should displace the half-wave potential by $+0.06$, *i.e.*, to $+0.31$ v (Found, see table : $+0.29$ to $+0.31$ v).

The second wave is caused by the reversible cathodic reduction of dissolved mercuric hydroxide (saturated solution $= 2.4 \times 10^{-4}$M. in water at 25°) :

$$Hg(OH)_2 + 2e \longrightarrow Hg + 2OH^-$$

The theoretical equation of the reduction wave of weakly dissociated mercuric hydroxide in the absence of excess of hydroxide ion (cf. the similar case of mercuric cyanide, Kolthoff and Lingane, " Polarography," Interscience Publ., New York, 1946, p. 181) is :

$$E_{d.e.} = E' - 0.0296\log_{10} I^2/(I_d - I)$$

Under the above conditions, the equation and half-wave potential depend only on the initial concentration of mercuric hydroxide at the electrode surface, and are independent (*e.g.*, in the case of partly neutralised hypochlorous acid solutions) of the pH value in the bulk solution.

Fig. 3 is the polarogram obtained with oxygen-free $0\cdot1\text{M}$-potassium nitrate, half saturated with yellow mercuric oxide at room temperature ($\simeq 10^{-4}\text{M}$.) and electrolysed at $25°$. A plot of $E_{\text{d.e.}}$ against $\log_{10} I^2/(I_{\text{d}} - I)$ gives a straight line of slope $= 0\cdot031$ (theory, $0\cdot0296$ v); similar agreement with theory is obtained on plotting data from Fig. 1. The half-wave potential obtained for $\simeq 10^{-4}\text{M}$-mercuric oxide agrees perfectly with the value for $\sim 10^{-4}\text{M}$-sodium hypochlorite ($+0\cdot10$ v.). The hypochlorite second half-wave potential decreases from $+0\cdot122$ (hypochlorous acid) to $+0\cdot099$ v. (sodium hypochlorite), save for the anomalous result at $36\cdot5\%$ neutralisation. This shift agrees qualitatively with the theoretical displacement of $0\cdot009$ v. on doubling of the concentration of mercuric hydroxide at the electrode surface. Hypochlorous acid in the presence of an equivalent amount of nitric acid (Fig. 1, curve A) shows no mercuric oxide wave; the observed polarogram owes its origin to the electroreduction of equal quantities of mercurous nitrate and calomel.

The above interpretations of the hypochlorite double waves were confirmed by examining the products of complete reduction by metallic mercury of (a) 10^{-4}M-sodium hypochlorite in $0\cdot1\text{M}$-potassium nitrate and (b) 10^{-4}M-hypochlorous acid in $0\cdot1\text{M}$-potassium nitrate containing $0\cdot2\text{M}$-acetate buffer (pH $5\cdot5$). In each case the polarogram of the soluble reaction products closely resembled that obtained with a similar solution without previous chemical reduction.

The nature of the electrode processes, elucidated above, does not of course invalidate the analytical applications of the dropping mercury electrode in hypochlorite chemistry : the overall cathodic limiting currents remain proportional to the bulk concentration of hypochlorite up to $5 \times 10^{-3}\text{M}$.