

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reduction of Iodate and Bromate at the Dropping Mercury Electrode in Neutral and Basic Media and the Effects of Salts upon the Current-Voltage CurvesBY E. F. ORLEMANN^{1,2} AND I. M. KOLTHOFF

Rylich³ found that the decomposition potentials of iodate and bromate ions observed in neutral or alkaline medium at the dropping mercury electrode are affected by the kind and concentration of indifferent salts in the solution. The decomposition potential becomes more positive with increasing valence of the cation and with increasing concentration of the salt. Rylich's data were not sufficiently extensive to allow a satisfactory interpretation of his results. In the present study we have made a systematic investigation of the effect of salts on the current-voltage (c. v.) curves of iodate and bromate in neutral or alkaline media, and an attempt has been made to devise a mechanism for the electroreduction of these ions which accounts for the experimental results. In a previous paper⁴ the c. v. curves of iodate and bromate in buffered solutions at pH values smaller than 8 have been reported.

Experimental

The manual apparatus was used as described in previous papers,⁴ and all the experiments were performed in a thermostat at $25.00 \pm 0.05^\circ$. The potentials were measured against the saturated calomel electrode (S. C. E.) at 25° . Two different capillaries of marine barometer tubing with the following characteristics were used: Capillary 2, pressure = 90 cm. of mercury; $m = 1.93$ mg. sec.⁻¹ at -0.6 v.; $t = 3.60$ sec. at -0.6 v.; $m^{3/4}t^{1/4} = 1.92$ at -0.6 v.; capillary 3, pressure = 80 cm. of mercury; $m = 1.80$ mg. sec.⁻¹ at -0.6 v.; $t = 3.52$ sec. at -0.6 v.; $m^{3/4}t^{1/4} = 1.79$ at -0.6 v. Changes of $m^{3/4}t^{1/4}$ with the potential of the dropping electrode were calculated with the aid of a table given in a previous communication.⁵ Current-voltage curves shown in the figures have been plotted without making correction for the residual current. The plots have been made using an exaggerated potential axis in order to avoid

crowding of the waves and to bring out small differences in the effect of the salt concentration. Values of the current used in the analysis of the waves and of the diffusion current reported in the tables have been properly corrected for the residual current of the particular medium used.

Effect of Alkali Salts and of Tetramethylammonium Bromide on the c. v. Curves of Iodate.—Salts were found to affect the relation between current and potential, the half wave potential, the value of K in the relation $i_d = Kc$, in which i_d is the diffusion current at a given potential and c the concentration of iodate. In addition, the change of the diffusion current with increasing negative potential was affected by the salt concentration. All the essential data are collected in a concise way in Table I. In all cases—with the exception of tetramethylammonium bromide—the equation of the wave was found to be given by the expression

$$\pi = \pi_{1/2} + a \log (i_d - i)/i \quad (1)$$

in which π is the potential and i the current at any potential on the wave. The value of a was obtained from the slope of the linear relation between $\log (i_d - i)/i$ and the potential. Examples of the linear relations found are given in Fig. 1. In this figure the plots obtained in 3.60, 0.91 and 0.09 M lithium chloride are shown. Values of a in the different salt solutions are listed in Table I.

In all cases—with the exception of tetramethylammonium bromide—the half wave potential (see equation 1) was found to be independent of the iodate concentration in a given salt solution. Values of $\pi_{1/2}$ are reported in Table I. The apparent diffusion current and the value of the potential at which it was obtained are listed in the column i_d at π . From the diffusion current and the concentration of iodate, also found in the table, the quantity $K_{ob} = i_d/c$ was obtained. The calculated value $K_{calcd.}$ was obtained from the Ilkovic equation

$$K_{calcd.} = i_d/c = 605nD^{1/2}m^{3/4}t^{1/4} \quad (2)$$

in which n is taken equal to six and $D = 1.09 \times 10^{-5}$ cm.² sec.⁻¹ at 25° .

The effect of the salt concentration on the change of the diffusion current with increasing

(1) From a thesis submitted by Edwin P. Orlemann to the Graduate School of the University of Minnesota in partial fulfillment of the requirements of the degree of Doctor of Philosophy, 1941.

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(3) A. Rylich, *Coll. Czechoslov. Chem. Commun.*, **7**, 288 (1935).

(4) E. F. Orlemann and I. M. Kolthoff, *This Journal*, **64**, 1944 (1942).

(5) *Ibid.*, **63**, 2083 (1941).

TABLE I
EFFECT OF SALTS ON C. V. CURVES OF IODATE

Salt	Salt concn., M	KIO ₃ × 10 ³ M	$\pi^{1/2}$ vs. S. C. E.	a in m. v. in eq. (1)	i_d obs. × 10 ⁶ amp. at -1.45 v.	i_d change with π	$K_{obs.}/K_{calcd.}$	$K_{cor.}/K_{calcd.}$	$D\Gamma O_3 \times 10^6$ cm. ² sec. ⁻¹
KCl	4.0	0.500	-1.150	85	17.10	Abn.	1.50	1.00	1.09
KCl	1.0	.500	-1.180	75	14.20	Abn.	1.25	1.00	1.09
KCl	0.5	.500	-1.195	75	12.20	Abn.	1.07		
KCl	.2	.500	-1.235		11.40	Norm.	1.00		1.09
KCl	.05	.500	-1.280	85	11.40	Norm.	1.00		1.09
KNO ₃	.2	.500	-1.230		11.30	Norm.	0.99		1.07
KNO ₃	.2	.100	-1.230		2.25	Norm.	.99		1.07
KNO ₃	.2	1.00	-1.230		22.5	Norm.	.99		1.07
CsCl	1.20	1.00	-1.155		20.7	Abn.	1.01		
CsCl	0.60	1.00	-1.170		20.5	Abn.	1.00		1.09
CsCl	.30	1.00	-1.190	70	20.8	Abn.	1.01		1.11
CsCl	.15	1.00	-1.220	65	20.4	Norm.	1.00		1.09
CsCl	.075	1.00	-1.240	65	20.3	Norm.	0.99		1.07
NaCl	3.60	0.91	-1.085	60	18.90	Abn.	1.02	0.73	0.58
NaCl	0.91	.91	-1.155	60	19.70	Abn.	1.05	.91	.90
NaCl	.09	.91	-1.270	65	18.80	Norm.	1.00		1.09
NaCl	.09	.375	-1.265		7.73	Norm.	1.00		1.09
LiCl	3.60	.91	-1.040	60	16.30	Abn.	0.875	.62	0.42
LiCl	1.80	.91	-1.090		18.15	Abn.	.970	.80	.70
LiCl	0.91	.91	-1.130	55	18.30	Abn.	.980	.86	.82
LiCl	.45	.91	-1.160		18.40	Norm.	.985	.975	1.03
LiCl	.09	.91	-1.215	60	18.65	Norm.	1.00	1.00	1.09
N(CH ₃) ₄ Br	1.80	.91	-1.280	80 ^x	16.50	Norm.	0.88	0.88	0.85
N(CH ₃) ₄ Br	0.90	.91	-1.270	70 ^x	17.90	Norm.	.96	.96	1.00
N(CH ₃) ₄ Br	.45	.91	-1.270	65 ^x	18.60	Norm.	1.00	1.00	1.09
N(CH ₃) ₄ Br	.09	.91	-1.300	65 ^x	18.50	Norm.	1.00	1.00	1.09

^x In tetramethylammonium bromide the equation of the wave is: $\pi = \text{Const.} - a \log(i_d - i)/i^2$.

negative potential is shown qualitatively in the column " i_d change with π ." According to the Ilkovic equation the ratio $i_d/m^{2/3}t^{1/6}$ in a given solution should be constant and independent of the potential. When this relation was found to hold the notation "Norm." is used in the column " i_d change with π ." At high salt concentrations the ratio $i_d/m^{2/3}t^{1/6}$ was found to decrease

markedly with increasing negative potential. In such cases the notation "abn." is used in the table. As a demonstration of the normal and abnormal effects we give in Fig. 2 the c. v. curves obtained in different concentrations of potassium chloride.

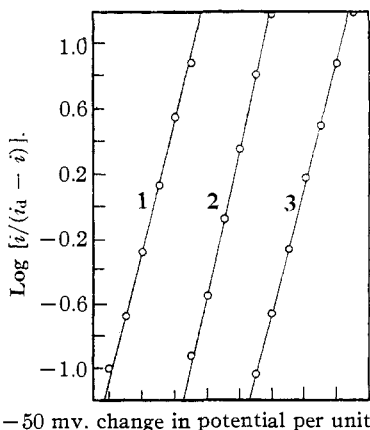


Fig. 1.—Analysis of the waves of iodate in lithium chloride solutions: Curves 1, 2 and 3 correspond to 3.6, 0.91 and 0.090 M lithium chloride, respectively.

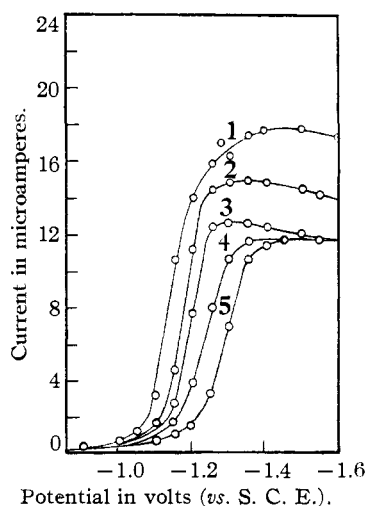


Fig. 2.—Current-voltage curves of 5×10^{-4} M potassium iodate in potassium chloride solutions of the following concentrations, using capillary 2: Curve 1, 4.0 M; curve 2, 1.0 M; curve 3, 0.5 M; curve 4, 0.2 M; curve 5, 0.05 M.

The cause of the abnormal change was found to be the occurrence of a "water current" at high salt concentrations. In a previous paper⁶ the conditions have been described under which such a "water current" occurs at high salt concentrations. In the present study it happens that this water wave overlaps with the iodate wave. Hence, the diffusion current observed is not the true diffusion current of iodate, but the sum of the latter and the water wave. That this interpretation is correct is demonstrated by the following figures. It has been shown⁶ that gelatin eliminates the water wave. Working with a $0.500 \times 10^{-3} M$ iodate solution in $4 M$ potassium chloride, we found a diffusion current of 14.6 microamp., which was reduced to 10 microamp. in the presence of 0.01% of gelatin. Similarly, in $4 M$ lithium chloride we measured a diffusion current of 9.7 microamp. which was reduced to 7.2 microamp. in the presence of 0.01% of gelatin.

From the data given in the paper on the water wave⁶ it was possible to calculate the magnitude of the water wave in the various salt solutions at a given potential. For the sake of brevity we will omit the various values and refer to the thesis of the junior author.¹ Only the final result is given in Table I in the column $K_{\text{cor.}}/K_{\text{calcd.}}$ in which $K_{\text{cor.}}$ is the experimental value of $K_{\text{obs.}}$ corrected for the water current. From the value of $K_{\text{cor.}}$ the diffusion coefficient of the iodate ion D_{IO_3} in the particular salt solution was calculated with the aid of equation (2), and is reported in Table I.

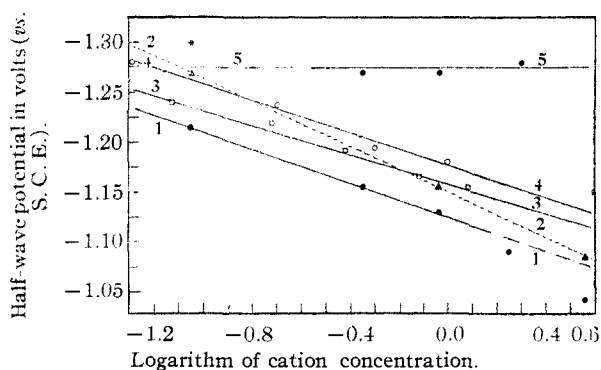


Fig. 3.—The relation between the half-wave potential of iodate and the concentration of cations in neutral or basic solutions at 25°: Curve 1, lithium ion; curve 2 sodium ion; curve 3, cesium ion; curve 4, potassium ion; curve 5, tetramethylammonium ion.

From the results reported in Table I the following conclusions are drawn: The observed and the

corrected diffusion currents are proportional to the iodate concentration in a given salt solution. When the salt concentration is smaller than $0.2 M$ the water current is negligibly small. Under such circumstances $i_d/m^{2/3}t^{1/6}$ becomes constant and independent of the potential or the " i_d change with π " becomes normal, while the calculated value of D_{IO_3} (equation 2) agrees exactly with the value of $1.09 \times 10^{-5} \text{ cm.}^2 \text{ sec.}^{-1}$ calculated from the mobility of the iodate ion at infinite dilution. It is of interest to notice that the diffusion coefficient of the iodate ion is not affected by the potassium chloride concentration. Even in $4 M$ potassium chloride it was found equal to the value at infinite dilution. On the other hand, the diffusion coefficient decreases markedly with increasing concentration of the other salts, the effect being $\text{LiCl} > \text{NaCl} > \text{Me}_4\text{NBr}$.

The relation between the half wave potential and the concentration of various univalent cations is shown in Fig. 3. Evidently, there is an approximately linear relation between the half wave potential and the logarithm of the concentration of the cation in the solution. The half wave potentials are necessarily somewhat uncertain as their measurement involves a liquid junction potential which cannot be corrected for in a satisfactory way. From Fig. 3 and the data in Table I the equations of the iodate waves and the characteristics of the waves were found. The corresponding data are summarized in Table II.

Effect of Divalent Cations on the c. v. Curves of Iodate.—The effects of barium and calcium chloride have been studied and the results are summarized in Table III. When the salt concentration is equal to or smaller than $0.1 M$, the normal value of the diffusion coefficient of the iodate ion is found. The latter decreases rapidly when the barium or calcium chloride concentration becomes greater than $0.1 M$. The equations and characteristics of the waves obtained upon graphical analysis are found in Table II. Again, there is a linear relation between the half wave potential and the logarithm of the barium or calcium concentration. We have tried to study the effect of trivalent cations on the iodate waves, but it was difficult to find ions which allowed an unambiguous interpretation of the c. v. curves. Salts of most trivalent cations are hydrolyzed and cause an acid reaction in the solution. In such cases the c. v. curves correspond to the "acid mechanism" of the iodate reduction⁴ or the re-

TABLE II
CHARACTERISTICS AND EQUATION OF IODATE WAVES IN UNIVALENT AND DIVALENT CATION SOLUTIONS (25°)

Salt	$\pi_{1/2}$ in 1 M salt	$\Delta\pi_{1/2}/\Delta$ log M, m. v.	Empirical equation of wave
LiCl	-1.125	85	$\pi = -1.125 + 0.08 \log [\text{Li}^+] + 0.06 \log (i_d - i)/i$
NaCl	-1.150	115	$\pi = -1.150 + 0.12 \log [\text{Na}^+] + 0.06 \log (i_d - i)/i$
KCl	-1.175	80	$\pi = -1.175 + 0.08 \log [\text{K}^+] + 0.08 \log (i_d - i)/i$
CsCl	-1.160	75	$\pi = -1.160 + 0.07 \log [\text{Cs}^+] + 0.06 \log (i_d - i)/i$
$(\text{CH}_3)_4\text{NBr}$	-1.275	0	$\pi = -1.275 + 0.07 \log (i_d - i)/i^2$ (i in μ amp.)
CaCl ₂	-0.940	50	$\pi = -0.94 + 0.051 \log [\text{Ca}^{++}] + 0.06 \log (i_d - i)/i$
BaCl ₂	-0.980	60	$\pi = -0.98 + 0.061 \log [\text{Ba}^{++}] + 0.06 \log (i_d - i)/i$

TABLE III
EFFECTS OF BARIUM AND CALCIUM CHLORIDE ON C. V. CURVES OF IODATE. CAPILLARY 3 WAS USED

Salt	Concn., M	$\pi_{1/2}$ vs. S. C. E.	a in m. v. in eq. (1)	i_d change with π	$K_{\text{obs.}}/K_{\text{calcd.}}$ at -1.4 v.	$K_{\text{cor.}}/K_{\text{calcd.}}$ at -1.4 v.	$D_{\text{IO}_3} \times 10^{-5}$ $\text{cm.}^2 \text{sec.}^{-1}$
BaCl ₂ ^a	1.50	-0.970	60	Abn.	0.90	0.72	0.56
BaCl ₂	0.75	-0.990	60	Abn.	.955	.92	.93
BaCl ₂	.37	-1.010	60	Abn.	.940	.93	.95
BaCl ₂	.187	-1.025	60	..	.920
BaCl ₂	.05	Norm.	.990	.99	1.07
CaCl ₂ ^b	5	(-0.800)	..	Abn.	.346
CaCl ₂	1	-.940	65	Abn.	1.04	.87	0.83
CaCl ₂	0.5	-.960	60	Abn.	1.02	.95	.99
CaCl ₂	.2	-.980	60	Abn.	1.03
CaCl ₂	.1	-.990	60	Norm.	1.01	1.01	1.11
CaCl ₂	.05	-1.005	60	Norm.	1.01	1.01	1.11

^a The iodate concentration in the barium chloride solutions was $0.91 \times 10^{-3} M$. The diffusion current was measured at -1.4 v. ^b The iodate concentration was $1.00 \times 10^{-3} M$.

duction takes place according to both the acid and neutral mechanism. Lanthanum salts of strong acids are practically unhydrolyzed. However, in this case a complication arises due to a film formation of lanthanum hydroxide on the mercury drop during the reduction and to the slight solubility of lanthanum iodate. Lanthanum salts shift the half wave potential markedly to more positive potentials. Examples of the striking lanthanum effect upon iodate waves in unbuffered solutions are shown in Fig. 4.

The solutions were 0.1 M in potassium chloride and $5 \times 10^{-4} M$ in iodate. In the presence of 0.1 to 0.01 M lanthanum chloride identical and steep waves were obtained (curves 1 and 2) with a half wave potential of -0.38 v. An equally steep wave was obtained in 0.001 M lanthanum salt (curve 3), but the half wave potential was shifted to -0.49 v. In 0.0001 M lanthanum solution (curve 4) the wave started at -0.6 v. and became poorly defined, probably as a result of precipitation of most of the lanthanum as hydroxide during the reduction of iodate. That the film of lanthanum hydroxide has some effect upon the shape and location of the wave is evident from a comparison of curves 2 and 5. Both solutions were

identical in composition except that the solution corresponding to curve 5 contained 0.01% of gelatin. The "decomposition potential" of the iodate

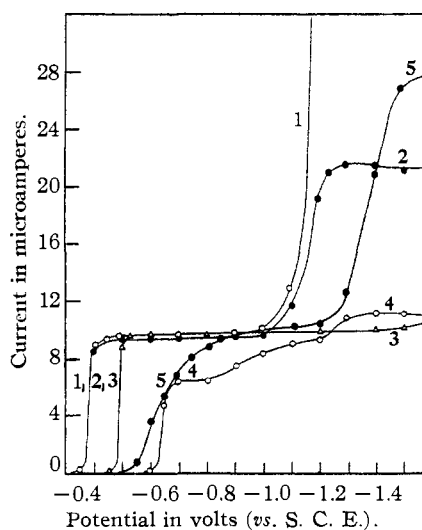


Fig. 4.—Current-voltage curves (using capillary 3) of $5 \times 10^{-4} M$ potassium iodate, 0.1 M potassium chloride solutions (unbuffered) in the presence of lanthanum chloride: The concentrations of lanthanum chloride are, curve 1, 0.1 M; curve 2, 0.01 M; curve 3, 0.001 M; curve 4, 0.0001 M; curve 5, 0.01 M lanthanum chloride with 0.01% gelatin present.

was shifted from -0.4 to -0.6 v. by the addition of gelatin. The drops of mercury falling in the diffusion current region in the absence of gelatin did not coalesce readily, presumably as a consequence of the presence of a film of lanthanum hydroxide, whereas they did coalesce in buffered

iodate solutions containing lanthanum. In addition in buffered solutions (pH 7) of lanthanum the iodate wave is found at a potential of the order of -0.8 instead of -0.4 v., indicating that the iodate reduction is catalyzed by the precipitation of lanthanum at the electrode.

Effect of Salts on the c. v. Curves of Bromate.—

Bromate is reduced at a much more negative potential than is iodate. Consequently, it is hardly possible to find well-defined diffusion currents in dilute solutions of alkali or barium salts, as the reduction of the alkali or barium ion sets in before the diffusion current is attained. In concentrated solutions of alkali salts, well-defined diffusion currents are found. Their values, however, are affected by the water current. For analytical purposes, therefore, it is not to be recommended to use concentrated solutions of alkali or barium salts as supporting electrolytes. Current-voltage curves obtained in solutions of potassium, barium and calcium chlorides are shown in Figs. 5, 6, and 7.

From Fig. 7 it is seen that, from the analytical viewpoint, dilute solutions of calcium chloride (0.025 to 0.2 M) are most suitable as supporting medium for the polarographic determination of bromate. Calculating from the mobility of the bromate ion at infinite dilution a coefficient of diffusion of 1.44×10^{-5} cm.² sec.⁻¹ at 25°, it was found that the values of i_d calculated with the aid of the Ilkovic equation (equation 2) agreed within 1 to 2% with the experimental data. The diffusion current was found proportional to the bromate concentration. For the sake of brevity we omit a complete account of all experimental data¹ and summarize the most important characteristics of the waves in Table IV.

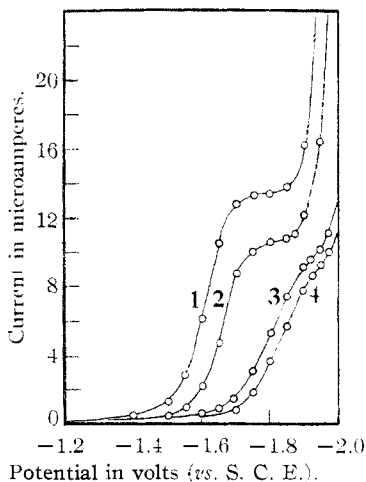


Fig. 5.—Current-voltage curves (using capillary 2) of 4×10^{-4} M potassium bromate in potassium chloride solutions of the following concentrations: Curve 1, 4.0 M ; curve 2, 1.0 M ; curve 3, 0.10 M ; curve 4, 0.05 M .

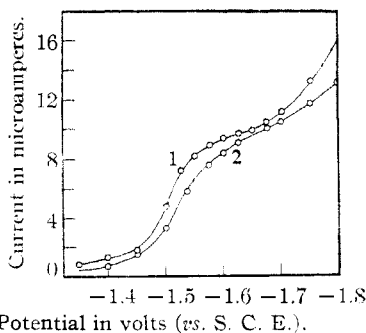


Fig. 6.—Current-voltage curves (using capillary 2) of 4×10^{-4} M potassium bromate in barium chloride solutions of the following concentrations: Curve 1, 0.165 M ; curve 2, 0.05 M .

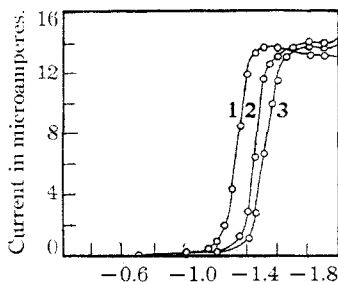


Fig. 7.—Current-voltage curves (using capillary 3) of 6×10^{-4} M potassium bromate in calcium chloride solutions of the following concentrations: Curve 1, 2.0 M ; curve 2, 0.4 M ; curve 3, 0.1 M .

TABLE IV

CHARACTERISTICS OF BROMATE WAVES IN SOME SALT SOLUTIONS

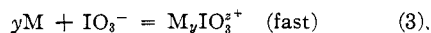
Salt	$\pi_{1/2}$ in 0.1 M salt	$\Delta\pi_{1/2}/\Delta \log$ cation in m. v.	Value of a in eq. (1) in m. v.
KCl	-1.780	115	60
CaCl ₂	-1.510	(150)	(90)
BaCl ₂	-1.555	(70)	100

Lanthanum chloride shifted the bromate waves to much more positive potentials. This is shown in Fig. 8. The solutions were 0.1 M in potassium chloride and 6×10^{-4} M in bromate. In the presence of 0.1 to 0.001 M lanthanum chloride identical and steep waves were obtained (curves 1, 2 and 3) at a potential of -0.82 v. The wave

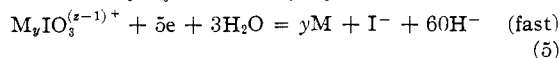
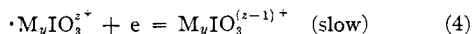
in 0.0001 *M* lanthanum solution (curve 4) was irregular probably as a result of exhaustion of lanthanum around the drop by precipitation as hydroxide. The solutions corresponding to curves 2 and 5 were identical (0.01 *M* lanthanum), except that the solution of curve 5 contained 0.01% of gelatin. The gelatin shifted the wave from -0.82 to -1.1 v.

Discussion

The linear relation between the half-wave potential and the logarithm of the concentration of cations noted in Fig. 3 and Tables II and IV shows that cations play a very definite part in the potential determining step involved in the reduction of iodate and bromate ions. A mechanism which accounts for this regular shift in half-wave potential with a change in concentration of cations has been developed by extending the ideas described in connection with the reduction of iodate and bromate ions in acid media.⁴ Considering only iodate, for convenience, the general mechanism proposed may be represented by the scheme



(in which *M* is the cation, *y* an integer, and *z* an integer depending upon *y* and the valence of *M*)



(this process probably occurs in several steps).

The above mechanism is identical with that proposed in connection with the studies in acid media if the cation *M* is taken as an hydrogen ion and the substance *M_yIO₃^{z+}* is iodic acid. In the discussion of the acid mechanism for the iodate and bromate reductions it was shown that if both iodate ions and a species such as *M_yIO₃^{z+}* coexist in a solution, it is easier to transfer an electron from the electrode into the species which has the lowest vacant electron level. If we make the reasonable assumption that the vacant electron level in *M_yIO₃^{z+}* is lower than it is in an iodate ion, then there will be a reduction of the former substance instead of a direct reduction of iodate ions. The reason for assuming that the slow step in the reduction is the transfer of one electron from the electrode to the iodate is discussed in the thesis of the junior author.

A quantitative formulation of the above mechanism readily can be made using the method of derivation given in the previous communication.⁴

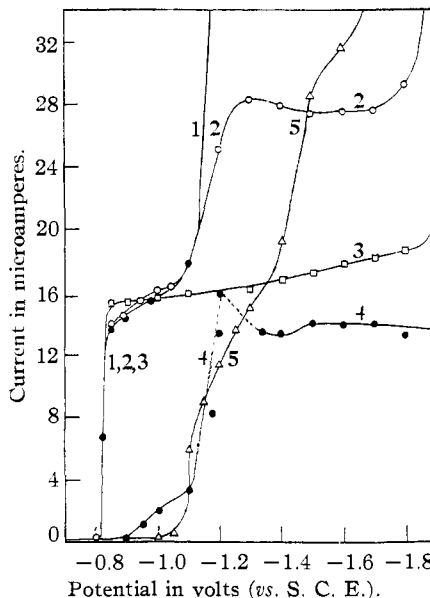


Fig. 8.—Current-voltage curves (using capillary 3) of 6×10^{-4} *M* potassium bromate, 0.1 *M* potassium chloride solutions (unbuffered) in the presence of lanthanum chloride. The lanthanum chloride concentrations are: Curve 1, 0.1 *M*; curve 2, 0.01 *M*; curve 3, 0.001 *M*; curve 4, 0.0001 *M*; and curve 5, 0.01 *M* lanthanum chloride with 0.01% gelatin present.

The equation for the c. v. curves found in this way is

$$\pi = \pi_{1/2} + \frac{RT}{\alpha F} \ln \frac{(i_d - i)}{i} \quad (6)$$

$$\pi_{1/2} = \text{const.} + \frac{RT}{2\alpha F} \ln \frac{i}{D} + \frac{RT}{\alpha F} \ln \frac{f_M^y f_{IO_3^-}}{f_{M_yIO_3^{z+}}} + \frac{yRT}{\alpha F} \ln [M] \quad (7)$$

In the above equations, α is the fraction of the total potential difference between the electrode and the bulk of the solution which acts in the reduction, *t* is the drop time, *D* is the diffusion coefficient of iodate ions, and *f* is the activity coefficient of the species indicated by the subscript used. The true definition of α is given in the previous communication,⁴ where it is shown that if the reduction occurs at a negatively charged surface the value of α would be expected to lie close to one. There was a variation of less than 5% in the drop time over the range of salt concentrations used in the experiments described. The diffusion coefficient of iodate ions varies with the salt concentration as shown by Table I. In the most extreme case shown in Table I, that of lithium chloride, the diffusion coefficient decreased approximately by a factor of two when the concentration of lithium chloride was increased from 0.1 to 4 *M*. In the concentration range from 0.1

to $4M$ it is difficult to find reliable data on the activity coefficients of the species involved and this factor will be neglected. To some extent the decrease in the diffusion coefficient tends to offset the decrease in activity coefficients in equation (7). The experiments reported were carried out at 25° and with the above considerations in mind equations (6) and (7) may be applied to the experimental data in the following approximate form:

$$\pi = \pi_{1/2} + \frac{0.060}{\alpha} \log \frac{(i_d - i)}{i} \quad (8)$$

$$\pi_{1/2} \cong \text{const.} + \frac{0.06y}{\alpha} \log [M] \quad (9)$$

From the experimentally determined slopes of the linear $\log (i_d - i)/i$ versus potential plots values of α were found with the aid of equation (8). Using the values of α determined in this way and the experimentally observed slopes of the linear relation between half-wave potential and the logarithm of the concentration of cations values of y were obtained with the aid of equation (9). Values of α and y determined in this way are shown in Table V. Since the reductions occur

TABLE V
VALUES OF α AND y IN EQUATION (7) IN THE IODATE
REDUCTION

Salt	$\frac{\Delta\pi_{1/2}}{\Delta \log (i_d - i)/i}$ mv.	$\frac{\Delta\pi_{1/2}}{\Delta \log M}$		y	Species reduced
		α	M, mv.		
LiCl	60	1	85	1.8 ^a	Li_2IO_3^+
NaCl	60	1	115	2	Na_2IO_3^+
KCl	60 (to 80) ^b	1	80	1	KIO_3
CsCl	65	1	75	1	CsIO_3
BaCl_2	60	1	60	1	BaIO_3^+
CaCl_2	60	1	50	1 (0.85)	CaIO_3^+

^{a, b} See text.

at a negatively charged mercury surface (see Fig. 3) the expected value of α is approximately one. With the exception of tetramethylammonium bromide this prediction is borne out. In the presence of tetramethylammonium salt the potential is not a linear function of $\log (i_d - i)/i$ but was found to be a linear function of $\log (i_d - i)/i^2$. We have not been able to find any reasonable explanations for this relation. In Table V values of 0.75 and 1 are listed for α in potassium chloride solutions. When the solution around the drop was suitably observed with a microscope during electrolysis in potassium chloride solution it was found that there was a stirring of the solution until the diffusion current was reached in those cases where the apparent value of α was 0.75. Addition of 2×10^{-3} per cent. tropeoline 00 to

these solutions completely eliminated this stirring and under these conditions the observed value of α was 1. In view of the approximate nature of equation (9) the values of y in Table V would be expected to deviate from unity. Taking this fact into consideration the values of y in Table V are reasonably close to an integral with the exception of those in lithium chloride solutions. In this case a better approximation of y was found by plotting the quantity

$$\pi_{1/2} + 0.03 \log D - 0.06 \log \frac{f_{\text{Li}^+} f_{\text{IO}_3^-}}{f_{\text{LiIO}_3^+}}$$

(see equation (7)) against the logarithm of the lithium chloride concentration. Values of the diffusion coefficient of iodate at the concentrations of lithium chloride used were found in Table I. It was assumed that $f_{\text{Li}^+}^2 f_{\text{IO}_3^-} / f_{\text{LiIO}_3^+}$ was equal to the mean activity coefficient of lithium chloride. The plot was found to be linear and the observed slope of 110 millivolts leads to a value of 1.8 for y which is reasonably close to an integral value of 2. To account for the observed values of y it is necessary to assume that the species being reduced in each case are those listed in the last column in Table V. The species BaIO_3^+ , CaIO_3^+ , KIO_3 and CsIO_3 listed in Table V appear reasonable but those listed with lithium and sodium do not.

The shift in half-wave potential with a change in drop time predicted by equation (7) was checked. At a drop time of 2.05 sec. the half-wave potential in 0.05 M potassium chloride was -1.256 v. and became -1.250 v. at a drop time of 4.10 sec. in the same solution. Therefore, the observed shift in half-wave potential with the above increase in drop time was 0.006 v. The shift calculated from equation (9) is 0.009 v., in reasonable agreement with the observed value.

The bromate reduction has been treated in the same manner as described above for the reduction of iodate and the results found are presented in Table VI. Qualitatively, the results in Table VI are in agreement with the mechanism proposed

TABLE VI
VALUES OF α AND OF y IN EQUATION (7) IN THE BROMATE
REDUCTION

Salt	$\frac{\Delta\pi_{1/2}}{\Delta \log (i_d - i)/i}$ mv.	$\frac{\Delta\pi_{1/2}}{\Delta \log M}$		y	Species reduced
		α	M, mv.		
KCl	60	1	115	2	K_2BrO_3^+
CaCl_2	80-100	0.75-0.6	(150)		(CaBrO_3^+)
BaCl_2	100	0.6	(70)	0.7	BaBrO_3^+
LaCl_3^a	100-140	0.6-0.4	90	0.6-0.9	LaBrO_3^{++}

^a Buffered solution.

but quantitatively they are not. The conclusion that there is a reduction of $K_2BrO_3^+$ is not reasonable although the other species indicated by the data in Table VI are acceptable. We are unable to give a reasonable quantitative explanation for these results on the basis of our present knowledge of the mechanism of electrolysis phenomena in general. In view of the qualitative and partial quantitative success of the proposed mechanism it seems reasonable to conclude that the mechanism is essentially correct but must be modified in some way to include secondary effects of cations, such as their effect on the detailed structure of the double layer

Some experiments were done in 50% acetone solution to see whether the expected increase in association of the ions in this medium would result in a change in the species which were apparently reduced. The relations observed between the half-wave potentials and the salt concentration in these cases are shown in Fig. 9. It is evident from Fig. 9 that the relation between these quantities is quite complex, but it is interesting to note that the half-wave potential is shifted with a change in concentration of tetramethylammonium bromide in this medium whereas it was practically unaffected by the concentration of tetramethylammonium bromide in aqueous medium. No attempt was made to extend these data or attempt an interpretation since too little is known about the behavior of concentrated salt solutions in 50% acetone.

Summary

1. In the reduction of iodate and bromate at the dropping mercury electrode in neutral or alkaline media, the following relation exists between the potential on the one hand and $(i_d - i)/i$

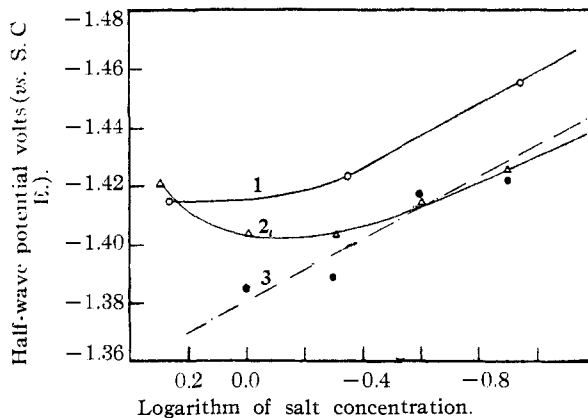


Fig. 9.—The half-wave potential of iodate as a function of the concentration of salt in 50% acetone solution. Curves 1, 2 and 3 correspond to solutions of tetramethylammonium bromide, potassium bromide and sodium chloride, respectively.

and the concentration of the indifferent cation M on the other

$$\pi = \pi_{1/2} + a \log(i_d - i)/i + b \log M$$

The relation does not hold in solutions of tetramethylammonium bromide. Values of a and b in the iodate reduction have been determined in solutions of varying concentrations of potassium, sodium, lithium, cesium, calcium and barium.

2. There is a linear relation between the shift of the half-wave potential and the concentration of the different cation in the solution (with the exception of tetramethylammonium ion).

3. The half wave potential is slightly dependent upon the drop time.

4. A mechanism has been proposed for the reduction of iodate and bromate in salt solutions. It has been postulated that in the case of iodate the following species are reduced: KIO_3 , $CsIO_3$, $Na_2IO_3^+$, $Li_2IO_3^+$, $BaIO_3^+$, $CaIO_3^+$.

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