

ent with the postulate of dipole-dipole bonds between oxygen and mercury in dioxane solu-

tions of the mercuric halides.

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The Anomalous Electroreduction of Water at the Dropping Mercury Electrode in Relatively Concentrated Salt Solutions¹

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In an investigation of the electroreduction of iodate and bromate ions, the results of which will be communicated in a subsequent paper, we found a marked increase in the "apparent" diffusion currents with increasing concentration of potassium chloride, when the concentration of this salt was greater than 0.5 *M*. A similar effect of the concentration of potassium chloride on the "apparent" diffusion current of other reducible ions was found. Further investigations showed that these, and some related, effects were due to an anomalous electroreduction of water molecules. By an electroreduction of a water molecule we mean the introduction of an electron directly into a water molecule to produce a hydrogen atom and an hydroxyl ion. The current resulting from this reduction process is called the "water current" and its characteristics and partial interpretation are discussed in this paper.

Experimental

The manual apparatus described in a previous communication³ was used. All experiments were carried out in a thermostat at $25 \pm 0.02^\circ$. Solutions were made up using reagent quality salts and conductivity water. The current measurements were precise to $\pm 1\%$, and the diffusion currents reported in this paper have been corrected for the residual current. Unless otherwise stated, the characteristics of the capillary used were: $m = 1.80$ mg./sec and $t = 3.50$ seconds at -0.6 v. (*vs.* S. C. E.) in 0.1 *M* potassium chloride. All potentials are based on the S. C. E. at 25° as a reference electrode.

The Anomalous c. v. Curve of Thallous Chloride in 4 *M* Potassium Chloride Solution.—In Fig. 1. the c. v. curves obtained with 0.001 *M*

thallous chloride in air-free 0.1 and 4 *M* potassium chloride solutions are shown. The residual current in 4 *M* potassium chloride is almost identical with that found in 0.1 *M* potassium chloride. Curve 2 has a normal appearance and the slight decrease in the diffusion current with increasing negative potential is due to a decrease in the quantity $m^{2/3}t^{1/6}$ with increasing negative potential.^{3,4} It is evident that practically the same diffusion current of thallium is found in 0.1 and 4 *M* potassium chloride solutions. In curve 3, however, the current begins to rise at -0.9 v. and increases with increasing negative potential until a maximum value is reached at a potential of the order of -1.35 v. When the potential is made more negative than -1.4 v., the current decreases and the decrease is much greater than that corresponding

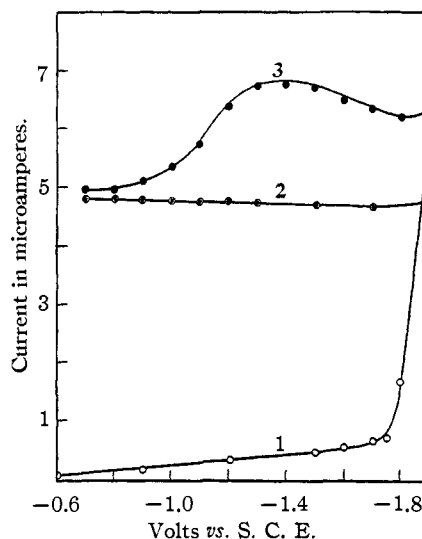


Fig. 1.—Current-voltage curves of thallous chloride in potassium chloride solutions: Curve 1 is the residual current in 4 *M* potassium chloride; Curve 2, 0.001 *M* thallous chloride in 0.1 *M* potassium chloride; Curve 3, 0.001 *M* thallous chloride in 4 *M* potassium chloride. Curves 2 and 3 have been corrected for the residual current.

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

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(3) J. J. Lingane and I. M. Kolthoff, *THIS JOURNAL*, **61**, 825 (1939).

(4) I. M. Kolthoff and E. F. Orlemann, *ibid.*, **63**, 2085 (1941).

to the decrease in $m^{2/3}i^{1/3}$ previously mentioned. The large increase in current at potentials more negative than -1.8 v. is due to a reduction of potassium ions. The wave which starts at -0.9 v. and continues until the reduction of potassium ions begins is the "water wave" which is considered in this paper. It is important to notice that curve 1, representing the c. v. curve of $4 M$ potassium chloride solution, does not show any reduction wave until the decomposition potential of potassium ions is reached.

Evidence for a Direct Electroreduction of Water Molecules.—The shape of the water wave, with its flat maximum, suggests that it might be due to a stirring at the surface of the drop. Frumkin⁵ and Antweiler⁶ have shown that the ordinary type of maxima found on c. v. curves are due to such a stirring. The use of a microscope to observe the solution around the drop showed no stirring during the water wave although a distinct stirring was visible at the thallium maximum (not shown in Fig. 1). A logical conclusion is that a reduction of water, according to the equation: $2\text{H}_2\text{O} + 2e = \text{H}_2 + 2\text{OH}^-$, occurs to a limited extent under the specified conditions. This conclusion has been verified by showing that the

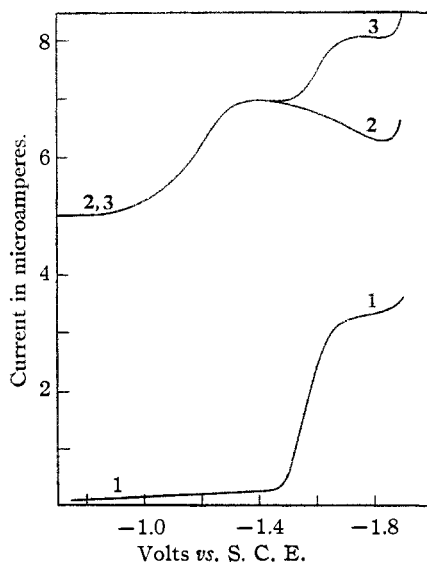


Fig. 2.—Schematic representation of the current-voltage curves of mixtures of thallos chloride and hydrochloric acid in $4 M$ potassium chloride solution: Curve 1, about $2 \times 10^{-4} M$ hydrochloric acid; Curve 2, $10^{-3} M$ thallos chloride; Curve 3, mixture of thallos chloride and hydrochloric acid.

(5) A. Frumkin and B. Bruns, *Acta Physicochim.*, U. S. S. R., **1**, 232 (1934).

(6) H. J. Antweiler, *Z. Elektrochem.*, **43**, 596 (1937); **44**, 719 (1938).

water current results in the formation of hydroxyl ions at the electrode surface.

Kolthoff and Miller⁷ have shown that the diffusion current of hydrogen ions in a given solution is decreased when oxygen is reduced in the same solution. Hydroxyl ions formed in the latter reduction combine with an equivalent amount of hydrogen ions diffusing to the electrode. For this reason the decrease in the diffusion current of hydrogen ions is exactly equal to the total diffusion current of oxygen. The formation of hydroxyl ions at the surface of the dropping mercury electrode thus manifests itself by a reduction of the diffusion current of hydrogen ions. We have made use of this principle in the present case.

In Fig. 2 are shown c. v. curves of thallos chloride and hydrochloric acid alone and in mixtures in $4 M$ potassium chloride solution. From curve 1, the diffusion current of hydrogen ions at -1.7 v. was obtained. The total "apparent" diffusion current, i_t , at -1.7 v. was found from curve 3. The diffusion current of thallium, i_{Tl} , was determined at -0.8 v. using curve 3. This value was corrected for the decrease in $m^{2/3}i^{1/3}$ (see Kolthoff and Orlemann⁴) to find the value of i_{Tl} at -1.7 v. The sum of $i_{\text{Tl}} + i_{\text{H}_2\text{O}}$ at -1.7 v. was obtained from curve 2 directly. By subtracting the value of $i_{\text{Tl}} + i_{\text{H}_2\text{O}}$ from i_t the value of i_{H} in the mixture of hydrogen and thallos ions was found. Subtracting i_{Tl} , at -1.7 v. from $i_{\text{Tl}} + i_{\text{H}_2\text{O}}$ at the same potential gave the value of $i_{\text{H}_2\text{O}}$ at -1.7 v. The data so obtained are listed in Table I. Considering that the quantities compared in the last two columns of Table I are the differences of much larger quantities, which are only known to $\pm 1\%$, it is evident that the hydrogen ion diffusion current in the mixture has been decreased by an amount equal to the water current.

TABLE I
EFFECT OF THE WATER CURRENT ON THE DIFFUSION CURRENT OF HYDROGEN IONS

i_t	$i_{\text{Tl}} + i_{\text{H}_2\text{O}}$	i_{H} Mixture	i_{H} Alone	Δi_{H}	$i_{\text{H}_2\text{O}}$ measured
6.53	5.95	0.58	2.12	-1.54	1.45
7.80	4.90	2.90	4.24	-1.34	1.20

Experiments similar to the above were done in hydrochloric acid solutions containing an excess of bromate. Under these conditions a diffusion current of hydrogen ions is obtained at -1.0 volt. Such experiments also lead to the conclusion that the hydrogen ion diffusion current is de-

(7) I. M. Kolthoff and C. S. Miller, *THIS JOURNAL*, **63**, 1013 (1941)

creased by an amount equal to the water current. These experiments are direct proof that the water current does produce hydroxyl ions to the amount of one mole of hydroxyl ion per faraday of electricity.

Curve 3 in Fig. 2 reveals the extremely interesting fact that the electroreduction of water molecules begins at a potential of the order of -0.9 v. whereas the electroreduction of hydroxonium (H_3O^+) ions does not occur until a potential of the order of -1.6 v. is reached. The above result means that under the conditions described the overvoltage required for the direct reduction of a water molecule is less than the overvoltage required for the reduction of an hydroxonium ion. The water current is observed to begin at a potential of the order of -0.9 v. in $4 M$ potassium hydroxide solution. The reversible potential for liberation of hydrogen gas at one atmosphere under these conditions is of the order of -1.08 volts. This apparent discrepancy of the order of 0.2 v. between the actual and the thermodynamically possible potential can be explained if the liberated hydrogen atoms form a very dilute amalgam in the mercury and do not form hydrogen molecules at the very small current densities prevailing during the beginning of the water wave. To check this explanation perchloric acid solutions were electrolyzed with a pool of mercury as a cathode and a platinum wire as an anode. The hydrogen amalgam so obtained was washed rapidly in conduc-

tivity water and immediately placed in the dropping mercury electrode. The c. v. curves obtained in this way showed an anodic wave corresponding to the oxidation of hydrogen in the amalgam to hydrogen ions. The potential at which the anodic wave of hydrogen occurred was found to depend upon the pH of the solution and very markedly upon the concentration of hydrogen in the amalgam. When the concentration of hydrogen in the amalgam gave an anodic diffusion current of 1 microampere the anodic wave of hydrogen was found at a potential of the order of -0.5 v. in $1 M$ potassium hydroxide solution. In view of this result it appears possible that the reduction of a water molecule to give a dilute hydrogen amalgam and an hydroxyl ion in $4 M$ potassium hydroxide can occur at a potential of -0.9 v.

Relation between the Water Current and the Total Current.—In the present section only the maximum value of the water current, represented by the symbol i_{H_2O} , is considered. The water wave only occurs when another current, due to the reduction of some constituent in the solution, passes. Therefore, corresponding to the maximum value of the water current, there is a relation: $i_t = i_{red} + i_{H_2O}$ where i_{red} is the diffusion current of the reducible constituent at the potential where the maximum value of the water current is found and i_t is the total current at this potential.

Table II shows that the ratio i_{H_2O}/i_t is constant and independent of the individual values of i_{red} and i_t if the characteristics of the capillary and the medium are kept constant.

Effect of the Kind and Concentration of Indifferent Electrolyte on the Water Current.—From the results in Table III it is evident that the water current occurs quite generally at high

TABLE II
CONSTANCY OF i_{H_2O}/i_t IN $TiCl_3 + 4 M$ KCl SOLUTION AT $\pi = -1.35$ v.

$i_t \times 10^6$	5.30	6.40	12.30	17.10
$i_{H_2O} \times 10^6$	1.40	1.70	3.00	4.30
i_{H_2O}/i_t	0.26	0.27	0.24	0.25

TABLE III
VALUES OF i_{H_2O}/i_t IN VARIOUS INDIFFERENT ELECTROLYTE SOLUTIONS AT 25°

Salt	Concn. M	π max. vs. S. C. E.	i_{H_2O}/i_{total} at π max.	Salt	Concn. M	π max. vs. S. C. E.	i_{H_2O}/i_t at π max.
LiNO ₃	2	-1.35	0.19	RbCl	4	-1.40	0.29
NaCl	4	-1.25	.28	RbCl	2	-1.40	.23
NaCl	1	-1.25	.13	RbCl	1	-1.40	.17
NaCl	0.5	-1.25	.01	RbCl	0.25	-1.35	.05
KCl	4	-1.35	.27	NH ₄ Cl	2	-1.30	.16
KCl	2	-1.35	.20	NH ₄ Cl	1	-1.30	.09
KNO ₃	2	-1.35	.16	NH ₄ Cl	0.5	-1.30	.01
KCl	1	-1.35	.14	Et NCl	4		.0
KCl	0.4	-1.35	.0	CaCl ₂	2	-1.35	.19
KOH	4	-1.35	.30	CaCl ₂	1	-1.35	.16
BaCl ₂	1.5	-1.35	.20	CaCl ₂	0.5	-1.30	.07
BaCl ₂	0.75	-1.35	.04	CaCl ₂	0.25	-1.30	.01
BaCl ₂	0.38	-1.35	.01				

salt concentrations. The experiments were carried out with solutions of thallos chloride.

The water wave was most pronounced in rubidium chloride solutions where it was noticeable even in 0.25 *M* solution. On the other hand, the water wave was not found in tetraethylammonium chloride solutions even when the concentration of this salt was 4 *M*. Otherwise, most of the salts of univalent cations behave very similarly.

Effect of Capillary Active Substances on the Water Current.—The striking effects of small amounts of various capillary active substances are evident from the curves in Fig. 3. Curve 2 in Fig. 3A shows that gelatin in a concentration as small as 0.005% eliminates the water current. Apparently, the presence of substances adsorbed on mercury prevent the water from coming close enough to the surface to be reduced. Gelatin still seems to be adsorbed on the mercury at the potential where potassium is discharged. On the other hand, tylose (curve 3 in Fig. 3A), which is often used as a maximum suppressor, seems to become desorbed at a potential of -1.6 v. In the presence of 0.01% of tylose the water current does not

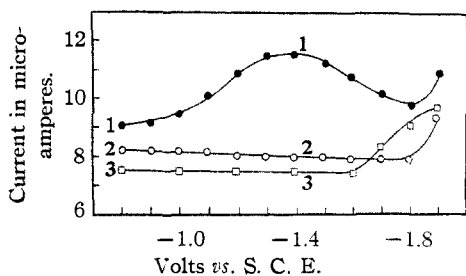


Fig. 3A.—Curve 1, 0.0018 *M* thallos chloride; Curve 2, 0.0016 *M* thallos chloride, 0.005% gelatin; Curve 3, 0.0015 *M* thallos chloride, 0.01% tylose.

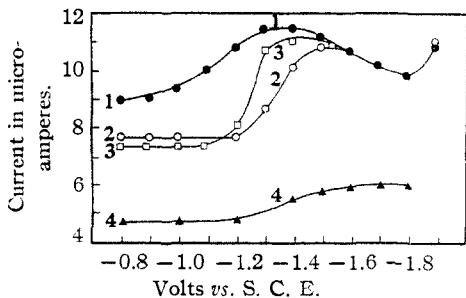


Fig. 3B.—Curve 1, 0.0018 *M* thallos chloride; Curve 2, 0.0016 *M* thallos chloride, 0.001% methylene blue; Curve 3, 0.0015 *M* thallos chloride, 0.02% camphor; Curve 4, 9.6×10^{-4} *M* thallos chloride, 0.001% tropeolin 00.

Fig. 3.—Effect of capillary active substances on the water current, in 2 *M* potassium chloride solutions.

occur until a potential of -1.6 v. is reached. Camphor (curve 2 in Fig. 3B) in a concentration of 0.02% shifts the beginning of the water wave from a potential of -1.0 to -1.3 v. In their studies of the polarographic behavior of cystine, Kolthoff and Barnum⁸ showed that camphor is suddenly desorbed at the mercury solution interface at a potential of about -1.3 v. Curves 3 and 4 in Fig. 3B show that methylene blue and tropeolin 00 behave similarly to camphor although the desorption of the former two extends over a greater range in potential than it does in the case of camphor. In this connection the fact that no water wave occurs in tetraethylammonium chloride solutions may be attributed to the strong adsorption of the tetraethylammonium ion on mercury. From a practical point of view the above results are important since they show that gelatin can be used to prevent completely the occurrence of the water current.

Effect of the Characteristics of the Capillary on the Water Current.—In Fig. 4, c. v. curves of thallos ions in 2 *M* potassium chloride solution at various values of the pressure on the capillary are shown. The occurrence of a thallium maximum was mentioned in connection with Fig. 1. A portion of this maximum appears on the curves of Fig. 4. The thallium maximum becomes more

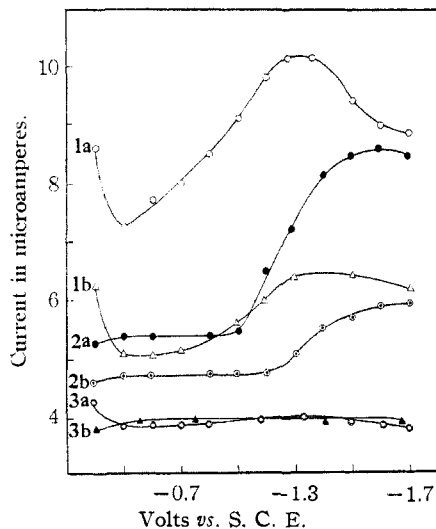


Fig. 4.—Effect of mercury pressure on the water current in 4 *M* potassium chloride solutions: Curve 1a, 0.001 *M* thallos chloride at a pressure of 100 cm. of mercury; Curve 2a, 0.001 *M* thallos chloride, pressure 75 cm.; Curve 3a, 0.001 *M* thallos chloride, pressure 50 cm. The above curves were repeated in the presence of 0.001% tropeolin 00 to give the curves marked with the subscript b.

(8) I. M. Kolthoff and C. Barnum, *THIS JOURNAL*, **63**, 520 (1941).

pronounced with increasing m and decreasing t , and under unfavorable conditions the current does not become equal to the diffusion current of thallium at the potential where the water current starts (curve la, Fig. 4). In order to find the true diffusion current of thallium in such cases the experiment was repeated in the presence of 0.001% tropeolin 00 which eliminates the thallium maximum (curve lb Fig. 4). Since tropeolin 00 affects the water current (see previous section) curves with the subscript b were only used to determine the diffusion current of thallium and curves with the subscript a were used to obtain the sum of the thallium and water currents (i_t) at a potential of -1.35 v. The results are reported in Table IV.

TABLE IV
EFFECT OF THE MERCURY PRESSURE ON i_{H_2O}/i_t AT 25° IN
2 M KCl

P, cm. Hg.	m , mg. sec. ⁻¹	t , sec.	$i_{Tl} \times 10^6$	$i_t \times 10^6$	i_{H_2O}/i_{total}
100	2.32	2.23	5.40	10.15	0.47
100	2.32	2.20	8.70	15.30	.44
80	1.85	2.75	9.70	12.52	.23
80	1.85	2.80	8.75	11.55	.24
75	1.73	3.00	4.70	6.40	.26
50	1.16	4.40	6.30	6.56	.04
50	1.16	4.50	3.85	3.93	.02

It is interesting to notice that the water current is practically eliminated when the drop time becomes 4.5 seconds or greater.

It was found that an equation of the type

$$i_{H_2O}/i_t = km^n t^{n-1} \quad (1)$$

gave the relation between the water current and the characteristics of the capillary. The data used are in Table V. Data with $m = 2.33$ and $t =$

TABLE V
RELATION BETWEEN i_{H_2O}/i_t AND m AND t AT 25°

KCl, M	m , mg./sec.	t , sec.	i_{H_2O}/i_t	k , $n = 0$	k , $n = -1/3$	k , $n = -2/3$
4	1.80	2.80	0.29	0.81	1.40	2.38
4	2.33	3.55	.19	.67	1.37	2.78
2	1.80	2.80	.23	.64	1.10	1.90
2	3.36	3.38	.14	.47	1.08	2.38

3.55 were obtained in this laboratory by W. E. Harris in a study of the reduction of uranyl chloride in 4 M potassium chloride solutions. The other data were obtained using thallos chloride in potassium chloride solutions of the indicated concentrations. The column headed k is the value of i_{H_2O}/i_t divided by $m^n t^{n-1}$ using the values of n listed. The values of n used were integral multiples of $1/3$ since the radius of the drop and its related functions, such as the area, would be ex-

pected to determine the ratio i_{H_2O}/i_t . It is obvious from Table V that k is constant in 4 M and 2 M potassium chloride only when $n = -1/3$. The relation between i_{H_2O}/i_t in a salt solution of constant concentration, and the characteristics of the capillary is therefore given by the relation:

$$i_{H_2O}/i_t = km^{-1/3} t^{-4/3} \quad (2)$$

Current-Voltage Curves at Stationary Mercury Electrodes.—From equation 2 it appears that the water current is greatly dependent upon the rate of formation of the mercury surface. The following experiments show that the water current does not occur when the area of the surface of the mercury is kept constant. The two electrodes used in these experiments are shown in Fig. 5. Electrode A in Fig. 5 has been described in detail by Laitinen.⁹ With these electrodes it is necessary to wait for a "steady state" at each value of the potential before a constant value of the current can be measured. This takes from three to five minutes. The c. v. curves obtained with these electrodes using thallos chloride in 4 M potassium chloride did not give any indication of the occurrence of a water current.

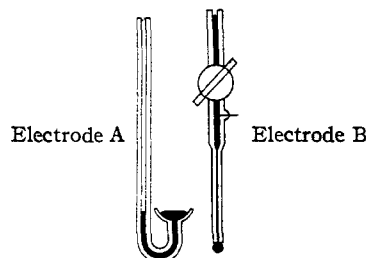


Fig. 5.—Stationary mercury electrodes.

Interpretation of the Water Current.—It has been shown that the water current only occurs at potentials more negative than -0.9 v. (vs. S. C. E.) when: (1) there is a relatively high electrolyte concentration, (2) a current due to the electroreduction of some species present in the solution is flowing in this potential region, (3) the mercury surface is increasing, and (4) strongly adsorbable substances, such as gelatin, are absent. To account for these facts we suggest the following explanation. The effect of the salt concentration is to compress the double layer which is created by the negatively charged mercury surface. As the double layer is compressed, with increasing salt concentration, the electric intensity between the mercury surface and the "adsorbed" cation layer in the solution is increased. When the electric in-

(9) H. A. Laitinen, Thesis, University of Minnesota, 1940.

tensity in this layer becomes sufficiently great, water molecules in the region right at the electrode surface are reducible due to their resultant polarization. Since the water current does not occur at the dropping mercury electrode in the absence of a current due to the electrolysis of some other substance, we conclude that the dense adsorbed cation layer acts to prevent ready access of water molecules to the electrode surface. Ilkovic¹⁰ has shown that the passage of a current requires the existence of an inhomogeneous electric field where the electric intensity increases rapidly as the surface of the drop is approached. In such a field water molecules, being dipoles, are acted upon by a force directed toward the electrode surface. The passage of a current is necessary therefore to bring water molecules into the adsorbed layer at the electrode surface where they are reducible.

The fact that the water current does not occur at stationary mercury electrodes leads to the conclusion that the inhomogeneous field can bring water molecules to the electrode surface in appreciable quantity only during the establishment of the double layer. Once the cation layer is established the number of water molecules reaching the electrode surface becomes negligible.

The water current is suppressed by capillary active substances because the latter act to prevent water molecules reaching the electrode surface and in addition change the structure of the double layer.

Quantitative Interpretation of the Water Current.—Let r be the distance from the center of the drop to a point in the solution. Let E be the electric intensity. Let μ be the effective dipole moment of the water molecule. If t_s is the time necessary to establish the double layer at 1 cm.² of mercury surface, and k_1 is a suitable proportionality constant, the number of moles of water which reach 1 sq. cm. of mercury surface during the establishment of the double layer would then be given by the relation:

$$\text{Number of moles of water per sq. cm.} = k_1 \mu \left(\frac{dE}{dr} \right) t_s \quad (3)$$

Denoting by $[d(\text{H}_2\text{O})/dt]_0$ the rate at which water molecules reach the mercury surface and by dA/dt the rate at which the surface increases with time, we have the relation

$$\left[\frac{d(\text{H}_2\text{O})}{dt} \right]_0 = k_1 \mu \frac{dE}{dr} t_s \frac{dA}{dt} \quad (4)$$

If $i_{\text{H}_2\text{O}}$ is the water current and F is the faraday, the rate of removal of water molecules is $i_{\text{H}_2\text{O}}/F$. Taking the rate of removal equal to the rate of supply yields

$$i_{\text{H}_2\text{O}} = k_1 F \mu \frac{dE}{dr} t_s \frac{dA}{dt} \quad (5)$$

According to Ilkovic¹¹ we have the relation

$$\frac{dE}{dr} = \frac{i_t}{2Kkr^3} \quad (6)$$

where i_t is the total current flowing and K is the specific conductivity of the solution.

Substituting Eq. 6 in Eq. 5 gives the relation

$$\frac{i_{\text{H}_2\text{O}}}{i_t} = \frac{k_1 F \mu t_s}{2\pi K r^3} \frac{dA}{dt} \quad (7)$$

When m is the mass of mercury per second flowing from the capillary and t is the drop time we find

$$\frac{i_{\text{H}_2\text{O}}}{i_t} = \frac{k_1 F \mu t_s k_2}{2\pi k_3 k} m^{-1/2} t^{-1/2} \quad (8)$$

At a constant salt concentration and at a given potential Eq. 8 may be written

$$\frac{i_{\text{H}_2\text{O}}}{i_t} = k m^{-1/2} t^{-1/2} \quad (9)$$

Equation 9 is identical with Eq. 2 which was empirically found.

Summary

1. It has been shown that the passage of a current in salt solutions of the order of 0.5 M or greater causes an electroreduction of water at the dropping mercury electrode. The water current is proportional to the total current flowing. The water wave found starts at a potential of the order of -0.9 v. (*vs.* S. C. E.), reaches a maximum value at about -1.35 v. (*vs.* S. C. E.) and then decreases markedly as the potential is made more negative. The relation $i_{\text{H}_2\text{O}}/i_t = k m^{-1/2} t^{-1/2}$ was found to hold where $i_{\text{H}_2\text{O}}$ is the water current, i_t is the total current, m is the mass of mercury per second, t is the drop time and k is a constant depending upon the potential and the kind and concentration of salt present.

2. Gelatin in a concentration of 0.01% suppresses the water current. The effect of other strongly adsorbed substances is described and interpreted.

3. A quantitative interpretation of the conditions necessary for the water current to occur has been given.

(10) D. Ilkovic, *Coll. Czechoslov. Chem. Commun.*, **8**, 13 (1936).